DEPORTATION OF TOXIC PHENOL FROM AQUEOUS SYSTEM BY WHEAT HUSK

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ABSTRACT: The potential of employing wheat husk for phenol adsorption from aqueous solution was studied. Batch experiments and isotherm studies were carried out under varying experimental conditions of contact time, phenol concentration, adsorbent dose and pH. The extent of removal was dependent on concentration of phenol, contact time, pH, and quantity of adsorbent. Adsorption equilibrium of wheat husk was reached within 5 hr for phenolic concentration 100-900 µg/L. With an initial concentration of 0.2 mg/L phenol in 100 mL and pH 7.0, the removal was found to be about 91.7% with 3.0 g wheat husk. The adsorption of phenol decreases 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 wheat husk was very effective at lower concentrations of phenol for removal. The studies showed that the wheat husk can be used as an efficient adsorbent material for removal of phenols from water and wastewater.
Keywords: toxics; phenol; removal; wastewater treatment; wheat husk

INTRODUCTION

Over the past several decades there is growing concern about wide spread contamination of surface and ground water by various organic compounds which are emitted due to the rapid development of chemical and petrol chemical industries. Many industrial wastes include organics which are difficult, or impossible to remove by conventional biological treatment processes [1]. Phenolic compounds which are common contaminants in wastewater and suspected as toxic and carcinogenic, are generated from petroleum and petrochemical, coal conversion and phenol-producing industries [2]. Phenols being harmful to organisms at low concentrations are considered as priority pollutants by USEPA [3] and European Union [4] 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 [3]. Whereas, the European Union (EU) lays down a maximum concentration of 0.5 µg L^{-1} for total phenols in drinking water [4]. Apart from their toxicity and carcinogenity, phenols being extremely soluble in water can cause bad taste and odor, even at low concentration [5]. The odor threshold for phenol is 0.04 ppm (U.S.EPA). In the presence of chlorine in drinking water, phenols form chlorophenol, which has a medicinal taste, which is quite pronounced and objectionable [6,7]. For these reasons it is essential to remove phenols from wastewater before it is discharged.

Various treatment technologies such as adsorption, photo-degradation, flocculation, chemical oxidation, biological process, *etc*. are available for the removal of phenol from the wastewater. Biological process is particularly suited to wastewater containing small amount of phenol. Oxidation is used when phenol concentration in wastewater is very high. In coagulation and flocculation process, large amount of sludge is generated which may cause disposal problems. Among various physicochemical processes, adsorption is a well-established and powerful technique for treating domestic and industrial effluents used for the removal of phenol from wastewater. There is abundant literature available on removal of phenolic compounds by adsorption onto activated carbon [2]. Activated carbons remove many of the impurities occurring in water and wastewater [8-10]. In spite of these characteristics, due to the relatively high cost of activated carbons and variable performance of carbon regeneration, there have been attempts to utilize economic, practical, efficient and naturally occurring adsorbents like bottom ash, brick-kiln ash, fly ash, peat, soil, wood, bagasse, carbonized bark, straw, auto mobile tires, fertilizer waste and saw dust [1,2]. However, the adsorption behaviour of phenol on wheat husk has not been extensively studied. Since, the main component of wheat husk is carbon, it has the potential to be used as an adsorbent [11]. According to April 2009 the world production of wheat was 682 million metric tons (Source: World production data sheet, USA: Foreign Agricultural Service, United States Department of Agriculture, http://www.fas.usda.gov).

Wheat husk is a lignocellulosic waste product which is about 15–20% of wheat and some extents of wheat husk uses as cattle food and fuel [12]. 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 [13]. The present study is intended to use this locally available agricultural waste as a conventional cheap material for phenol adsorption. The influences of various factors, such as initial pH and initial pollutant concentrations on the sorption capacity were examined. The Freundlich and langmuir models were used to analyze the adsorption equilibrium.

MATERIALS AND METHOD
The wheat husks (Figure 1) used in the study was obtained from the central region of Indore. The proximate and ultimate analysis of wheat husks are shown in Table 1. The wheat husk was sun dried, crushed and sieved with a 30-mesh sieve. Then, the husks were thoroughly washed with distilled water to remove all dirt and were dried at 100ºC till constant weight. The dried husks were stored in desiccator until used. The test solutions were prepared by diluting stock solution of phenol to the desired concentrations. The stock solution was obtained by dissolving 1.0g of phenol, (obtained from Merck), 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 (0.1 to 0.9 mg/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 CL120, ChemiLine. Sorption studies were conducted in a routine manner by the batch technique. Each phenol solution was placed in 250 ml conical flasks and a known amount of wheat husk (1 to 9g) was added to each flask. 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 wheat husk, before analysis, samples were distilled by distillation apparatus according to standard methods [14]. Then, distilled samples analysed for the remaining phenol. The studies were performed at room temperature to be representative of environmentally natural condition. 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.
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 digital ultra violet-visible spectrophotometer equipment (spectrophotometer Model-371, EI). The absorbance of the colored complex of phenol with 4-aminoantipyrine was read at 500 nm [14].

RESULTS AND DISCUSSION
The adsorption of phenol in aqueous solution on wheat husk was examined by optimizing various physicochemical parameters such as; pH, contact time, and the amount of adsorbent and adsorbate.

Effect of Initial pH: In any adsorbate-adsorbent system, pH of the system affects the nature of surface charge of the adsorbent, effects ionization, the extent of rate of adsorption and speciation of the adsorbate species. The adsorption of phenol on various adsorbents has been studied at different pH values [7,15-19]. Measurement of initial and final phenol concentration gave the percent adsorption of phenol. The results are displayed in Figure 2. Adsorbed amount decreased with increasing pH value, which can be attributed to the phenol ionization to form phenolate ions and at the same time the presence of hydroxyl ions on the adsorbent prevents the uptake of phenoate ions [16]. Similar behaviour has been reported during the adsorption of phenol onto tendu leaf refuse and modified carbon prepared from tendu leaf refuse by Nagda *et al*., [19]. Mustafa *et al*., [2] studied the removal of phenol by jute stick in aqueous system. He found that the uptake with 40 ppm phenol was small at low pH ranges and gradually increased up to pH 10.0, where maximum removal 68% occured. In our study the decrease in adsorbed phenol was sharp at pH 9.

The ionic fraction of phenolate ion φ_{ions} can be calculated from [3]

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

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 [3,20]. 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 [6,20].

Similar behaviour has been reported by Halouli and Drawish [16] for the adsorption of phenol by activated carbon, adsorption of phenol onto bentonite by Banat *et al.*, [3] and onto tendu leaf refuse modified carbon by Nagda *et al.*, [19]. 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 [6,15].

Effect of Contact Time: The adsorption data for the uptake of phenol versus contact time at 150μg/L initial concentration with 5g wheat husk was carried out at pH value of 7. The results show that equilibrium time required for the adsorption of phenol on wheat husk was almost 5hr. The 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 120 min of adsorption as also observed by Mahvi *et al.*, [1], Mustafa *et al.*, [2] and Kermani *et al.*, [21]. Figure 3 shows the effect of contact time on the removal of phenol by wheat husk.

Influence of Adsorbent Dose and Initial Phenol Concentration: Batch experiments were carried out to investigate the effect of phenol concentration on the extent of adsorption as a function of time for the initial phenol concentration of 0.1-0.9 mg/L and 10 mg/L. The amount of adsorbent on the efficiency of adsorption was also studied. Figure 4 shows the removal of phenol by wheat husk at the solution pH of 7. Adsorbent dosage was varied from 1g to 9g for wheat husk. The results show that for removal of 0.1 mg/l of phenol in 100 ml of solution, a minimum dosage of 9 g of wheat husk is required for 73% removal of phenol. But, with this condition removal of phenol at 10mg/l in 100 ml of solution by wheat husk, the removal efficiency is 62.2%. It is evident that for the quantitative removal of different value of phenol in 100 ml a high dosage of wheat husk is required. The equilibrium sorption capacities of the sorbents obtained from experimental data at different initial phenol concentration are presented in Figure 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. On a relative basis, however, the percentage adsorption of phenol decreases (Figure 4) as the initial phenol concentration increases. The data clearly shows that the wheat husk is more effective adsorbent at lower concentrations of phenol than at higher concentrations.

Adsorption Isotherms: It essentially expresses the relation between the concentrations of the solute in solution at dynamic equilibrium with the concentration of the solute adsorbed onto the adsorbent at constant temperature. Several models have been published in the literature to describe experimental data of which the most common are the Langmuir isotherm and the Freundlich isotherm [22].

In order to facilitate the estimation of the adsorption capacities at various conditions, the Langmuir adsorption isotherm, a typical model for monolayer adsorption was applied. The linearized Langmuir model can be written as [1,3,6,15,19]:

$$\frac{1}{qe} = \frac{1}{Q^0} + \frac{1}{bQ^0}\frac{1}{Ce}$$

Where: $Q°$(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 slope of the linear plot experimental data of $1/qe$ versus $1/Ce$ [1,3,6,15,19]. The Freundlich isotherm has been widely adopted to characterize the adsorption capacity of organic pollutants using different adsorbents by fitting the adsorption data. The Freundlich isotherm in its linearized form can be written as [1,3,6,15,19]:

$$\ln qe = \ln K + \frac{1}{n}\ln Ce$$

Where: qe is the amount adsorbed of equilibrium (mg/mg), Ce is the equilibrium concentration of the adsorbate (mg/L), and K and $1/n$ is the Freundlich constants related to adsorption capacity and adsorption intensity respectively, of the sorbent. The values of K and $1/n$ can be obtained from the intercept and slope, respectively, of the linear plot of experimental data of ln qe versus ln Ce [1,3,6,15,19].

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 wheat husk.

The linearized Freundlich and Langmuir adsorption isotherms of each sorbent for phenol are shown in Figure 5 and Figure 6. The Langmuir and Freundlich constants are displayed in Table 2.

Table 1: Properties of Wheat husk

Proximate analysis (wt %)		Ultimate analysis (wt %)		Component analysis (wt %)	
Volatiles	68.51	Carbon	43.2	Cellulose	39.2
Moisture	6.05	Hydrogen	5.0	Hemi cellulose	26.4
Ash	9.30	Oxygen	39.4	Lignin	6.8

Table 2: Parameters of Freundlich and Langmuir Isotherm Models

	Freundlich constants			Langmuir constants		
	K	1/n	R^2	Q^0	b	R^2
Wheat husk	0.0026	0.202	0.923	0.0022	15.83	0.903

The results reveal that the adsorption of phenol on wheat husk obeys the Freundlich adsorption isotherm. In general, R^2 Values, which are a measure of goodness-of-fit (Table 2), show that both the Langmuir and Freundlich isotherm models can adequately describe the adsorption data. The higher value of k, the Freundlich constant, showed easy uptake of phenol from aqueous solution [6,15,16]. The n value, which reflects the intensity of sorption, presents the opposite trend, but as seen from Table 2 for the sorbent and pollutant, n values were found high enough for separation. The higher fractional value of $1/n$ ($0 < \frac{1}{n} < 1$) signifies that the surface of the wheat husk is heterogeneous in nature [1,20]. 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 comparable to adsorption capacity as observed in Freundlich isotherm. A large value of b also implies that strong bonding of phenol occurred with sorbent [1,23]. 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 [3,6,20,23,24,25].

Figure 1. Wheat husks employed for the study
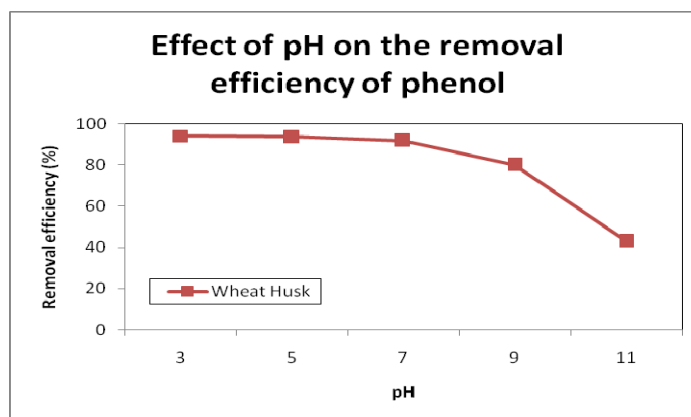
Figure 2. Effect of pH on the Removal of Phenol by Wheat Husk (Wheat Husk Dosage = 3 g/100 ml, Phenol Concentration = 0.2 mg/L)
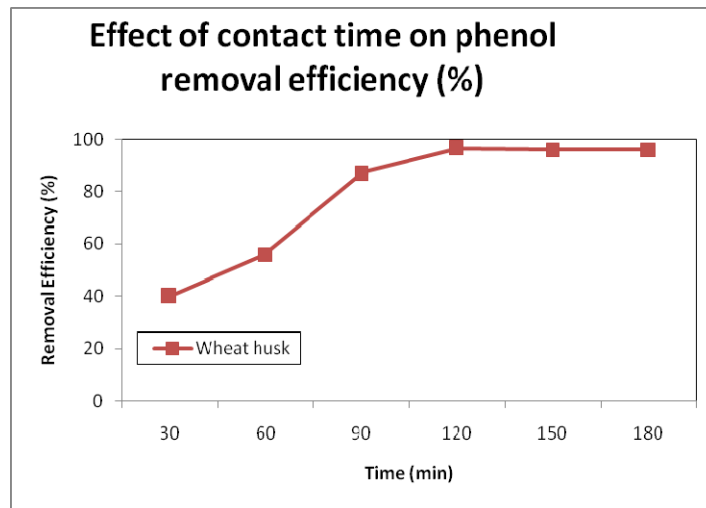
Figure 3. Effect of Contact Time for the Removal of Phenol by Wheat Husk (Wheat Husk Dosage = 5 g/100 ml, Phenol Conc. = 0.15 mg/L)
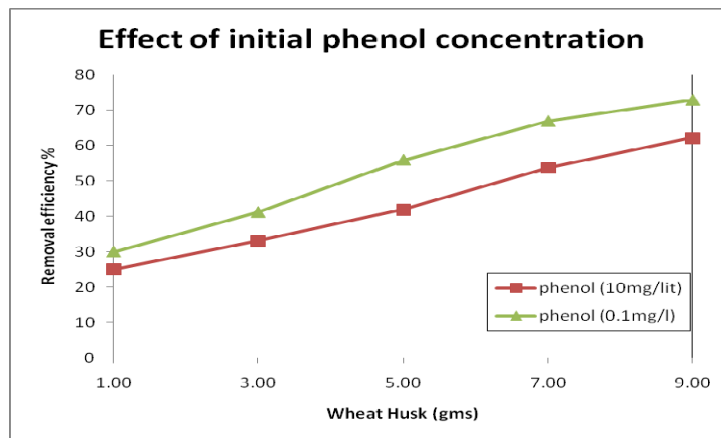

Figure 4. Effect of Wheat Husk on the Removal of Phenol for Various Initial Phenol Concentrations
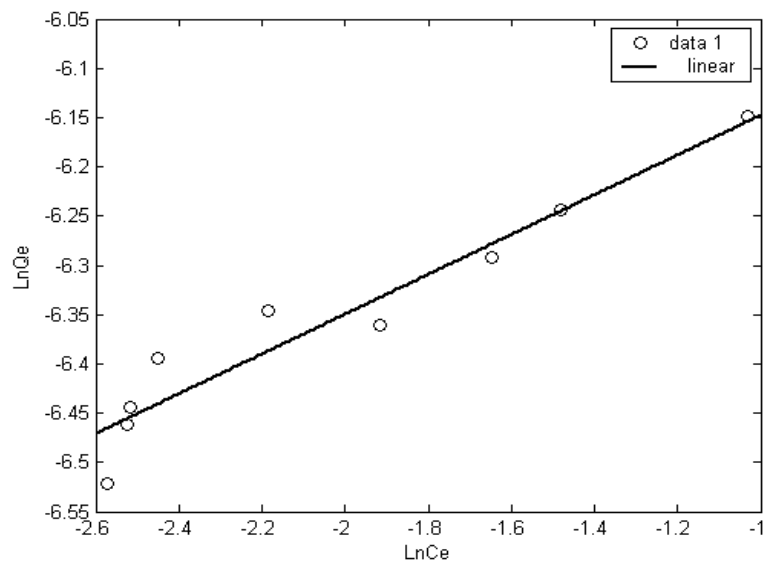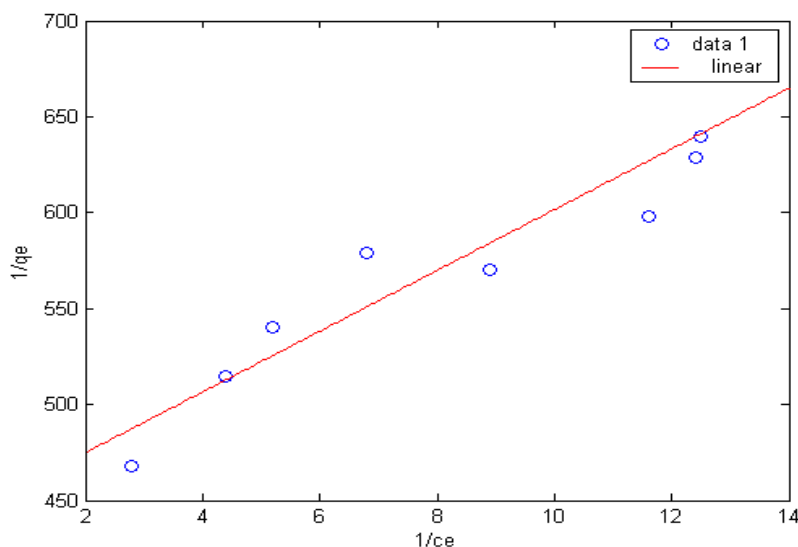

Figure 5. The Linearized Freundlich Adsorption Isotherm for Phenol with Wheat Husk

Figure 6. The Linearized Langmuir Adsorption Isotherm for Phenol with Wheat Husk

CONCLUSION

Arising from the results of this investigation the following conclusions can be drawn:

- In the present study, the ability of wheat husk to bind phenol was investigated as a function of pH and initial phenol concentration.
- Wheat husk adsorption capacity was strongly influenced by the pH of the solution
- Under batch conditions equilibrium was attained in 5 hr.
- Freundlich Langmuir adsorption models expressed the sorption phenomena of phenol to the wheat husk. Consequently, linear regression of the experimental data showed that the Freundlich equation best represented phenol adsorption data.
- The data clearly exhibits that the wheat husk is more effective adsorbent at lower concentrations of phenol than at higher concentrations.
- On the basis of this study, it may be concluded that wheat husk, may be used as low-cost, natural and abundant sources for the removal of low concentration of phenol.

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