

Original Article

The evaluation of removal efficiency of phenol from aqueous solutions using *Moringa Peregrina* tree shell ash

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Abstract

Background and purpose: Phenol is one of prevalent contaminants found in many industrial wastewaters. The combination with special features, such as high toxicity, carcinogenic properties, vitality gathering ability, low biodegradation potentiality and others, based on the U.S Environmental Protection Agency, classified as a priority pollutant. The purpose of this study was to determine the efficiency of *Moringa Peregrina* tree shell ash for the removal of phenol from aqueous solutions.

Materials and Methods: This study is experimental and pilot scale. To determine the efficiency of *Moringa Peregrina* tree shell ash for the removal of phenol from aqueous solutions; the examination was carried out in a batch system. To achieve the aim of this study, the effect of each of the parameters affecting the adsorption process, such as initial pH of solution, contact time, adsorbent dose and initial concentration of phenol in solution were studied.

Results: The results showed that the highest percentage of phenol removal by the ash occurred at pH 6, initial concentration 100 mg.L⁻¹ and adsorbent dose 0.4 g/l in which the 79.96% phenol was removed. For the analysis of the absorption constant, the Freundlich and Langmuir isotherm were used. The results showed that the experimental data fit the Langmuir ($R^2=0.9833$) much better than the Freundlich model ($R^2=0.9373$).

Conclusion: According to the results of this study, it was found that the *Moringa Peregrina* tree shell ash is not only a low-cost adsorbent but also has a high performance in the removal of phenol from aqueous solutions.

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Key words: Phenol Removal, Adsorption, Aqueous Solutions

1. Introduction

One of the major forthcoming challenges of human being is providing healthy water for the large population all over the world. This need is an important issue especially in the developing countries. Water resources are always prone to different contaminations due to anthropogenic and natural actions, which we should rapidly return them into the usage cycle regards to the shortage of water resources (1,2).

Phenol has an especial importance among the contaminating materials of water (3). Phenol is one of the most frequent contaminators in waste water of producing resin, plastic, yarn, petrochemical, coal, ceramic, glue, iron, steel, aluminum, leather, food process and etc. Furthermore, phenol is used as a solvent, disinfectant and an additive to increase the effectiveness of disinfectant (2-9).

Phenol is an inflammable composition with a high solubility in water and many other organic solvent (10). The presence of phenol in water causes malodor and bad taste. Also entrance of phenol in drinking water resources disinfected by chlorinated compositions cause's chlorophenol combinations. These materials cause medicinal taste and smell in water and make it inappropriate to use and revealed to protest of users. Also, phenol is potential human carcinogen and is of considerable health concern, even at low concentration. Owing to their toxic effects, including permeabilisation of cellular and cytoplasmic coagulation, phenolic contaminants can damage sensitive cells and thus cause profound health and environmental problems (7, 11-13). According to the classification of United State Environmental Protection Agency (USEPA), phenol compositions are among the prior combinations. This agency considered a concentration of less than 1 mg/L in the output of the filtered waste water to the superficial water, due to the potential effects of contacts to phenol (14). Institute of Standard and Industrial Research of Iran (ISIRI) considered the maximum allowed concentration of phenol introducing to the superficial water as 1 mg/L. Also according to the guides of World Health Organization (WHO), the

maximum allowance of phenol in drinking water is 0.002 mg/L (15).

So, diagnosis, determination and measurement of the phenol combinations in waste water containing these materials and eliminating them from industrial waste water before introducing into the water resources seem necessary. Up to know different methods are applied to eliminate phenol combinations from the water environmental like biologic filtration by ultrasound waves, photocatalytic destruction, membranous filtration, enzymatic filtration, and extraction by solvent, chemical oxidation, light oxidation, photochemical destruction and wet oxidation (11-16,29).

Most of these techniques have especial failures like high operative and device costs, needs for additive chemical substrate, high energy consumption, needs to further space and producing mug and toxins (30,31).

Adsorption process is one of the most common methods widely used for elimination of organic and non-organic contaminations from the water resources. Adsorption process is one of the most simple, effective and cost benefit alternative methods to phenol removal from aqueous environments (32-35). Active carbon, silica and active aluminum are used as the absorbent (36) but problems like high costs and the possibilities of activation and reclamation of the absorbent which are important from economic point of view, provoke investigators to search for new absorbents (37). At the present time, biomass draws increasing interest all over the world because it is a renewal material which is available widely with low costs and no damage to the environment (38). *Moringa Peregrina* seed is one of the desert type restricted growth in the southeast of Sistan and Balouchestan in Iran, and North Africa and southwest of Asia. *Moringa oleifera* seed usually grows in the upper mountain slopes where the surface is covered by rocks rubble (39). So, in this study the effective removal of phenol from aqueous solutions with the activated carbon from *Moringa Peregrina* tree shell was evaluated.

2. Methods

2.1. Preparing phenol solution

All chemicals used for this study are of Analytical grade (AR) and are obtained from Merck Company. Stock solutions of phenol were prepared by dissolving the required amount of phenol (99.9% purity) in deionized water without pH adjustment. Working solutions of the desired concentrations (10, 20, 30, 40, 50, 80 and 100 mg/L) were obtained by successive dilutions.

2.2. Method of measuring Phenol concentration

The residual phenol concentration in the solutions was determined using UV-spectrophotometer (Model T80 UV/VIS) by analyzing the color resulting from the reaction of phenol with 4-aminoantipyrine at maximum wavelength $\lambda = 500$ nm (41). Solutions with concentration higher than that detected by spectrophotometer were determined by dilution. The pH of solution was measured using a pH-meter (WTW, Germany).

2.3. Adsorbent preparation

Dry Moringa Peregrina tree shells were collected around the vicinity of Nikshahr city, Sistan and Baluchestan province, Iran. This natural wastes were firstly washed with distilled water to remove impurity such as sand and leaves and soluble and colored components, dried at 110 °C for 2 h, crushed in a domestic grinder and sieved to obtain particle size in the range of 60–200 mesh. Then a mixture of 250 g of powdered adsorbent, 110 g of ZnCl₂ and 110 g of water was kept overnight, and then the mixture was calcinated at 350°C. Then, chemically prepared activated carbon was washed with water and dried. The activated carbon was then used in adsorption experiments. No other chemical or physical treatments were used prior to adsorption experiments.

2.4. Batch adsorption experiments

For the phenol removal activated carbon obtained from Moringa Peregrina tree shell was used in a closed environment in Shaker 250 ml Erlenmeyer flask and magnetite shaker. Each test consisted of 100 ml of desired phenol concentration and pH of the dilution of phenol

stock solution prepared with distilled water. To adjust the pH, the concentration of phenol solution was then poured into the pH meter by using solutions of HCl and NaOH 0.1 N.

A known mass of Moringa Peregrina tree shell ash (adsorbent dosage) was then added to the solution, and the obtained suspension was immediately stirred for a predefined time. After the desired contact time, the samples were withdrawn from mixture by using a micropipette and the mixtures were then filtered through Whatman 42 filter paper and the concentration of phenol in the filtrates was analyzed. Then the amount of phenol adsorbed, q_e (m/g), was obtained as follows:

$$(1) \quad q_e = \frac{(C_0 - C_e)V}{M}$$

Which C_0 and C_e are primary phenol concentration and secondary one after the tests and reaching to the balance. V is the volume of solution (L) and M is the used amount of adsorbent (g). The following equation shows the rate of phenol elimination as percent:

$$(2) \quad \% = \frac{(C_0 - C_f)}{C_0} \cdot 100$$

In the above equation C_0 and C_f respectively show the initial and final concentrations (after adsorption) of phenol. All experiments were performed at room temperature 23 ± 2 °C and for sure repeated twice. Final results are reported as the average of the two measurements.

2.5. The effect of initial pH

The effect of initial pH on the removal of phenol from synthetic solutions was examined. The adsorbent used was 0.04 g in 100 mL of test solution and the initial phenol concentration in all samples was 50 mg/L. The initial pH of samples in each set of experiments was in the range of 2–12. Samples were put on magnetic shaker of 120 rpm for 60 min to make sure of balance. After the elapse time, they were filtrate by Whattman filter paper and the phenol concentration was measured

by spectrophotometer and results were analyzed. The above test was done in temperature between 23 ± 2 °C and repeated twice then the Final results are reported as the average of the two measurements.

2.6. The effect of absorbent dosage

Adsorption experiments to determine the effect of adsorbent dose on the removal of phenol from gaz ashes oily skin adsorption dose was done in a range of 0.01 to 0.07 g per 100 mL of a solution containing 50 mg/L at the optimal pH of 6 and contact time of 60 minutes at 23 ± 2 °C. Samples were taken after the shaking and the elapsed time as smooth and level were analyzed.

2.7. The effect of exposure time

To measure the effect of exposure time on adsorption process, tests were done in different times (15, 30, 60, 90, 120, 150, 180 and 210 min) for the primary phenol concentration of 50 mg/L in pH=6 and 23 ± 2 °C. 0.03 mg of adsorbent dissolved in 100 mL of the present solution in Erlenmeyer 250 mL flask and mixes the samples after exposure to the Shaker and the elapsed time then it was filtered as mentioned earlier and analyzed. Adsorption experiments continued to determine the effect of initial phenol concentration at pH =6 and 23 ± 2 °C. In this stage 0.03 grams of adsorbent were mixed in 100 mL of solution containing different phenol concentrations (10, 20, 30, 40, 50, 80 and 100 mg/L) and solutions exposed to the absorbent for 60 min with a rate of 120 rpm on the shaker. Then samples were filtered and analyzed as mentioned before.

3. Results

3.1. The effect of initial pH on adsorption effectiveness

PH of the solution is one of the most critical parameters that affect the chemical properties of absorbing and adsorbing (42). This parameter is directly appropriate with the competition ability of hydrogen ions with pollutants on the active surface of absorbent. So, phenol adsorption was studied as a function of hydrogen ion concentration to determine the optimal pH for phenol adsorption by ash.

Figure 1 shows the effect of initial pH value of the solution (in the range of pH=2-12) on the efficiency of adsorption of phenol by Ash with a concentration of 0.4 g/L initial phenol concentration of 50 mg/L respectively.

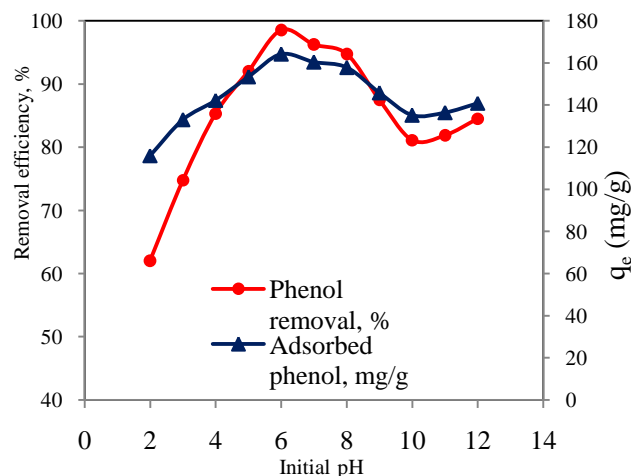


Figure 1. Effect of initial pH on the adsorption of phenol onto activated carbon obtained from Moringa Peregrina tree shell (Phenol concentration = 50 mg/L; adsorbent dose = 0.4 g/L; contact time = 60 min)

3.2. Effect of adsorbent dose on the phenol removal

The absorptive capacity of the adsorbent dose is one of the most important parameter for determining the initial phenol concentration; therefore, to determine the effect of adsorbent dosage on the adsorption process, the adsorbent dose in the range of 0.7 to 1 g/L and the initial phenol concentration of 50 mg/L, in pH =6 and 23 ± 2 °C temperature in 60 minute time period considered.

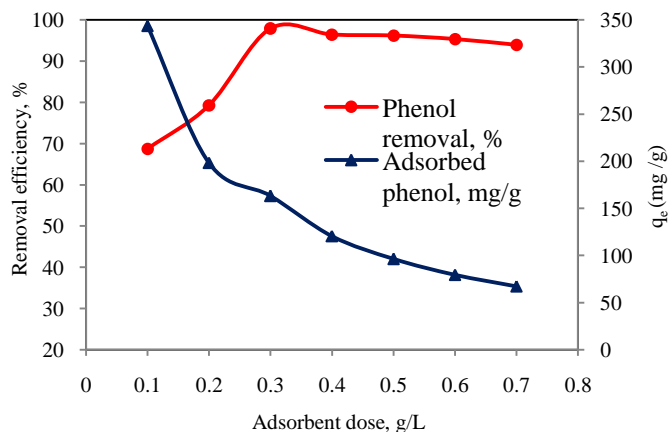


Figure 2. Effect of adsorbent dose on the adsorption of phenol onto activated carbon obtained from Moringa Peregrina tree shell (Phenol concentration = 50 mg/L; pH= 6; contact time = 60 min)

3.3. The effect of exposure time on efficiency of adsorption process

Exposure time is one of the most important parameters for the adsorption process to reach equilibrium. Effect of contact time on the adsorption process at a temperature of 23 ± 2 °C, initial phenol concentration, adsorbent dose of 50 mg/L and 0.3 g, were studied for a contact time 15-210 minutes.

Figure 3 shows the effect of exposure time on the adsorption capacity and the percentage of phenol elimination in primary phenol concentration of 50 mg/L. The adsorption capacity and percentage of phenol elimination is increased significantly at the first stages of adsorption and reached to a balance after 45 minutes. The elimination percentage reached to 98.04% and adsorption capacity to 163.4 mg/g, so it was chosen as the equilibrium time.

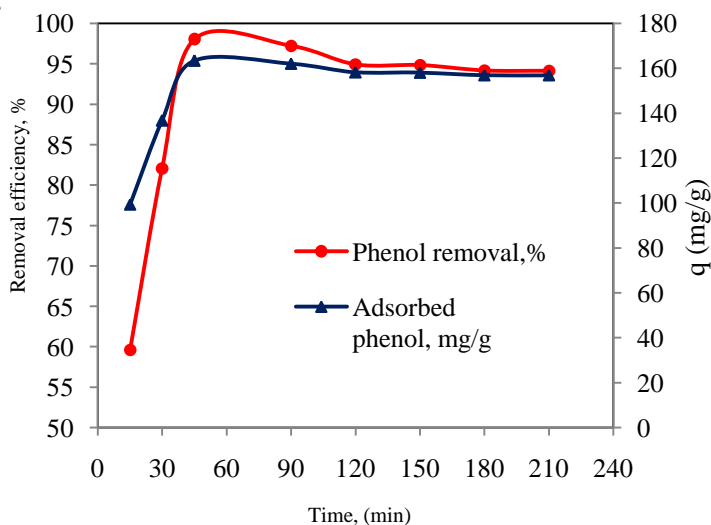


Figure 3. Effect of contact time for the adsorption of phenol onto activated carbon obtained from Moringa Peregrina tree shell (Phenol concentration: 50 mg/L, pH: 6, adsorbent dosage: 0.3 g/L)

3.4. The effect of primary phenol concentration on the effectiveness of adsorption process

The effect of primary phenol concentration on the efficiency of adsorption in temperature 23 ± 2 °C and adsorbent dose of 0.3 g/L for 45 min exposure time. As shown in figure 4, phenol adsorption rate will be increased by phenol concentration, so phenol elimination depends on its concentration.

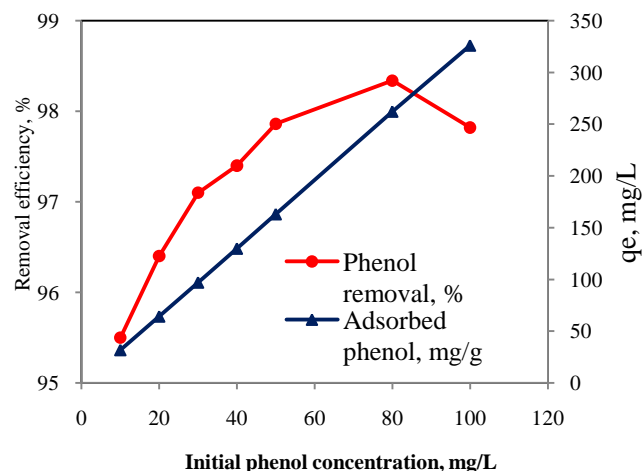


Figure 4. Effect of initial phenol concentration for the adsorption of phenol onto activated carbon obtained from Moringa Peregrina tree shell (pH=6, adsorbent dosage: 0.3 g/L and contact time=45 min)

3.5. Adsorption isotherms

Studying of isotherms could explain the reactions between adsorbent and adsorptive. Isotherm shows the relation between soluble phenol concentration and the rate of adsorbed phenol by the solid phase, when the two phase are in balance. Figures 5 and 6 show the balanced isotherms for phenol adsorption by Moringa Peregrina and data of balanced adsorption analyzed with Freundlich and Langmuir isotherms. Langmuir isotherm model is valid for monolayer adsorption onto surface containing finite number of identical sorption sites which is presented by the following equation:

$$(3) \quad q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$$

In the above equation, q_e stands for the adsorbed phenol in a certain amount of adsorbent (mg/g), C_e is for the balance concentration of solution (mg/L) and q_m is the maximum amount of phenol needed to form a layer (mg/g). Langmuir equation could change to linear model to facilitate drawing and achieving Langmuir constant (K_L) and the maximum adsorption of a layer of Moringa Peregrina (q_m). K_L and q_m could be achieved by linear drawing of $\frac{1}{q_e}$ in contrast to $\frac{1}{C_e}$.

(4)

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L} + \frac{1}{C_e}$$

The Freundlich equation is purely empirical based on sorption on heterogeneous surface, which is commonly described by the following equation:

(5)

$$q_e = K_f C_e^{\frac{1}{n}}$$

K_f and $\frac{1}{n}$ are the constant of Froondlich and respectively are dependent to the adsorption capacity and the severity of adsorption. Evaluating the constant of Froondlich equation is obtained from crushing the slope of linear figure, $\log q_e$ in contrast to $\log C_e$ based on tests. Below equation could be written as a linear logarithm to mention Freundlich constant.

(6)

Isotherms are shown in figures 5 and 6 based on laboratory data and measured parameters due to non linear regression for both models. Also all parameters are shown in Table 1. The correlation coefficient of Langmuir ($R^2=0.9672$) was higher than Freundlich model ($R^2=0.9448$) which shows that the Langmuir model is more appropriate to conclude the balanced adsorption of phenol on the adsorbent.

Table 1. Isotherm parameters for phenol adsorption onto activated carbon obtained from

Langmuir isotherm			Freundlich isotherm		
q_m ($mg\ g^{-1}$)	K_L ($L\ mg^{-1}$)	R^2	K_f	n	R^2
122.17	0.48	0.9672	122.69	0.63	0.9448

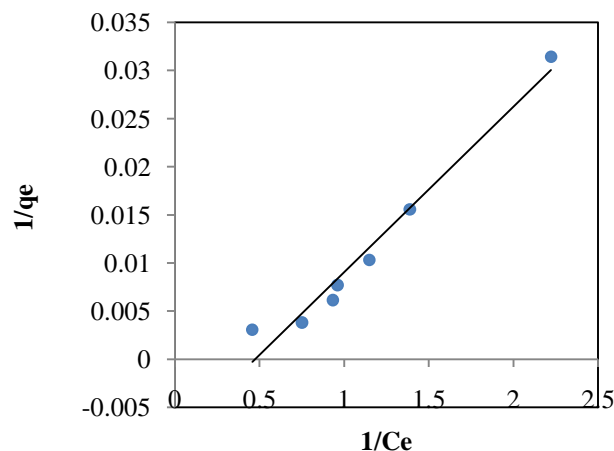


Figure 5. Langmuir isotherm for sorption of phenol onto activated carbon obtained from Moringa Peregrina tree shell ($R^2=0.9672$)

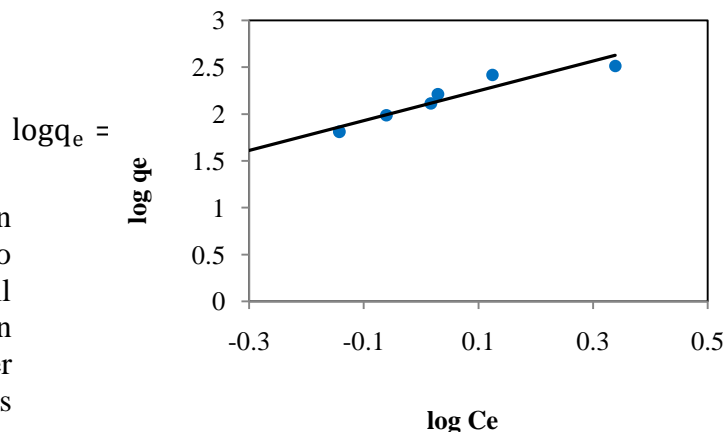


Figure 6. Freundlich isotherm for sorption of phenol onto activated carbon obtained from Moringa Peregrina tree shell ($R^2=0.9448$)

4. Discussion

PH of solution is one of the most effective parameter on the effectiveness of adsorption process which could lead to better or worse effectiveness of contamination elimination. As shown in figure 1, evidences show that after increasing pH to higher than 6, the effectiveness of phenol elimination will increase up to 98.54% and will be constant up to pH=7, then it will decrease. The most adsorption capacity of activated carbon obtained from Moringa Peregrina

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tree shell was 164.23 mg/g in pH=6. pH of phenol containing solution is effective on their adsorption via active carbon and in higher pH the adsorption rate will decrease (pH>7) because phenol is in the salty form which lose its negative load and phenol adsorption would be difficult. In addition OH⁻ ion presentation will inhibit the adsorption of phenol ions by absorbent. In lower pH and the presence of H⁺ ions will neutralize phenol ions and the adsorption on polar adsorption will decrease (43).

As it is shown in figure 2, phenol elimination depends on the absorbent amount in solution and will increase with increasing absorbent dose. It means that the phenol elimination percent will increase with a slight slope up to 0.3 g/L of absorbent dose. It would seem that there will be areas on the absorbent surface remained unsaturated during the adsorption process but the adsorption locations could be increased by increasing the absorbent dosage. The optimal elimination rate of phenol is 97.86 % (163.1 mg/g) which is achieved by 0.3 g/L of absorbent.

As shown in figure 2, when absorbent dose reached more than 0.3 mg/L, a dramatic increase would not seen in the elimination rate of phenol by absorbent. So it seems that after increasing the absorbent dose to a certain dose, the highest rate of adsorption would be achieved and after that the remaining contamination amount will be constant even after increasing dose (44). Although the elimination rate of phenol will be increased with increasing dose of absorbent, but the amount of absorbed phenol for each gram of absorbent will be decreased, because phenol concentration in the solution (50 mg/L) will be decreased due to adsorption by activated unsaturated areas of absorbent surface and increasing adsorption also causes aggregation of particles (45). So the amount of 0.3 g/L absorbent was considered as the optimal dose of absorbent for the next tests. Among other effective parameters on the adsorption process is the exposure time of adsorbent and adsorbate. According to the results of present study, totally the elimination rate of absorptive substance was rapid at first but decreased until the equilibrium time. This could be explained that at the first stage of adsorption the numbers of free spaces available on the absorbent surface are more, and then due to the

repulsion force between the absorptive molecules and the remained free surface of soluble phase, it would be harder. On the other hand, at first the percentage of phenol elimination is high due to available surfaces of absorbent to absorb contaminations. As the surface adsorption sites become exhausted, the rate of uptake is controlled by the rate of transport from the exterior to the interior sites of the adsorbent particles (44). Similar findings are reported by Cengiz and Cavas (46) and SenthilKumar et al (47).

The initial concentration of pollutants is an important driving force to overcome the deterrent mass transfer between liquid and solid materials adsorb provides (48). Actually, the primary phenol concentration is an important activator to overcome the inhibitory force of phenol germ between liquid and solid phase, so increasing the primary concentrations could increase the phenol adsorption capacity. These results are in concordance with other investigations (46, 48).

For example, when the initial phenol concentration increases from 10 to 100 mg/L adsorption equilibrium concentration of adsorbent increases from 31.83 mg/g (95.5%) to 326.07 mg/g (97.82%). The increase in the rate of phenol removal is probably due to balance changes during the adsorption process. Similar findings for the adsorption of methylene blue on activated carbon, bamboo, cotton waste and escaped ash is achieved. In addition, a similar result has also been recorded for adsorption of Congo red from aqueous solution onto calcium-rich fly ash (49-52). In this study it was observed that this adsorbent can be used effectively for the removal of phenol from aqueous solutions. Removal rate depends on pH, amount of adsorbent, contact time and initial concentration of phenol exposed to the adsorbent. The adsorbent can remove more than 97% of phenol from aqueous solutions with an initial concentration of 10 to 100 mg/L. Phenol adsorption Freundlich and Langmuir isotherms on adsorbents can be interpreted. The results showed that the Langmuir adsorption equilibrium of phenol on the adsorbent is more suitable for interpretation. Removal of phenol from aqueous solutions at low concentrations of phenol by adsorption on active surfaces of the absorber and the high concentrations of phenol by adsorption on surfaces and internal transactions occur.

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