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Contributed Paper

Agrowaste Based Ecofriendly Bio-adsorbent for the Removal of Phenol: Adsorption and Kinetic Study by *Acacia tortilis* Pod Shell

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ABSTRACT

Phenolic compounds are generally organic pollutants because of their toxicity even at low concentrations and lead to many hygienic and environmental problems. In this study, *Acacia tortilis* as a low cost and ecofriendly bio-adsorbent was investigated for phenol removal from aqueous solutions. Adsorption study were performed in a batch system, and the effect of important operation variables including the initial phenol concentration, adsorbent dose in predetermined sizes, pH, contact time, temperature and ionic strength were evaluated. The experiments showed that the maximum efficiency capacity for phenol adsorption was above %95, which was seen at the pH of 2, adsorbent dose of 0.1 gr/l, 60-100 mesh, contact time of 10 min, temperature of 45°C and high concentration of pollutant. Also the increase in the salt concentration resulted in a decrease of phenol adsorption onto Acacia tortilis pod sell. The equilibrium data could be described well by the Freundlich isotherm equation and the kinetic studies indicated that the adsorption process was best described by the pseudo-second order kinetics. According to the results the pod shell of *Acacia tortilis* due to its high efficiency can act as an effective, efficient and cheap adsorbent in removal of phenol from water and wastewater.

Keywords: phenol removal, agrowaste, *Acacia tortilis*, adsorption isotherm, kinetic

1. INTRODUCTION

Nowadays, the existences of non-degradable toxic chemicals in the environment have been led to hygienic and environmental problems. Phenol and phenolic compounds are among these chemicals, and due to its toxic and carcinogenic effects, have attracted the concern of many environmental specialists. The US Environmental Protection Agency (US EPA), has classified phenol among the type one pollutants [1]. Phenol (C_6H_6O) with a molecular weight of 94.11gr/M is a cyclic aromatic hydrocarbon and a derivative of benzene, and when pure, is a colorless white solid. It is in the form of colorless and water adsorbent crystals and after oxidation in contact with air, turns to pink. After dissolving in water, it shows weak acidity. Its dissolvtion in water is between 93-98 gr/l and dependents on water temperature (22 to 25°C) and its boiling point is 181°C. Phenol has weak acidic characteristics [2]. Phenolic compounds are hydrocarbons in which in their molecular structure, the hydroxyl group has made a link with the carbon atom of the benzene ring [3]. Phenol is produced naturally from coal tar and distillation of gasoline and is made artificially by heating sodium benzene sulfate with sodium hydroxide in high pressures [4]. Phenol naturally enters to environment through the degradation of algae and plants, but the existence of this chemical in surface waters is generally as a result of contamination with industrial wastewater [5]. This chemical and its derivatives are used in several industries including resin, plastic, dye, pesticide, drug manufacturing, oil refinery, petrochemical, coal mining, steel, aluminum and lead production, detergents, artificial goods and leather making industries and therefore is recognized as an important pollutant in mentioned industries' waste water. Phenol can also be found in disinfectants, detergents, cigarette smoke and exhaust smoke [6].

Phenol does not remain in the environment for long time, but if it is continuously released, it can act as a threat for the environment. Therefore, recognizing, identifying and determining the amount of phenol compounds in the environment and particularly in water resources and environment surveillances afterwards has high significance in controlling the dissemination of these chemicals and reducing the effect of these pollutants in the environment [7]. WHO has established the concentration of 0.001 mg/l in drinking water as the maximum permissible concentration for phenol. Moreover, according to the standards of the US Environmental Protection Agency (EPA) the permissible amount of phenol is in the drinking water resources 1-2 μg/l and industrial effluents 500 μg/l [3,5]. Up to now, different methods have been used for treating wastewater with phenol contamination and among them chemical, advanced and combined photochemical oxidation processes, precipitation, ion exchange, distillation, electrochemical methods, radiation, photo catalyst destruction, enzyme removal and adsorption had been studied [6]. Most of these methods have disadvantages such as the high cost of treatment, the necessity of extra treatment, the production of hazardous by products and low yield, and applicability for limited concentrations of pollutants [4]. Among the treatment techniques, adsorption is one of the efficient and effective techniques in separating toxic pollutants from aqueous environments [7]. Studies have shown that activated carbon is effective in adsorbing many organic pollutants from aqueous systems. US EPA advised activated carbon adsorption has been advised as one of the best available technologies for removing organic compounds. However, due to the high price and the barriers of re-reduction, its application in developing and low income countries has been limited. Therefore, this problem results in more research for finding cheap and locally available adsorbents for substituting activated carbon for removing different organic chemicals such as phenol [2].

In this study, for the first time Acacia tortilis pod shell was used as an available, ecofriendly, new and low cost adsorbent for the phenol removal. This plant is one of the most popular tree species in dry and semi dry environments which grow in North Africa, the Arabian Peninsula and parts of southern Iran. This plant is resistant to dry climate and is very resistant to flooding. This plant is a main food source for animals and is also used as firewood and is a suitable shelter for desert travelers. Performed studies on the branches and fruits of this tree in the Research Center for Agriculture and Natural Researches of Iran showed that the young branches include %6.16 protein, %4.2 fat, %3.18 fibers, %8.65 ashes, %0.72 calcium and %0.21 phosphorus [8,9]. The present study aimed to evaluate the efficiency of Acacia tortilis pod shell as a natural adsorbent in removing phenol from aqueous environments. Furthermore, the effect of various environmental factors such as pH, initial phenol concentration, adsorbent dose and its size, contact time, temperature and ionic strength on the adsorbing capacity was studied. Eventually, the sorption capacity of the adsorbent was studied by using adsorption isotherm technique. Finally, the kinetics of phenol adsorption was studied by using different models.

2. MATERIAL & METHODS

2.1 Materials and Instrumentation

All chemicals used in this study were reagent grade and were used without further purification except deionized water which was used as the solvent. A hot air oven and a desiccator were used for drying and storing adsorbent, respectively. An electrical mill and a standard ASTM sieve were used for grinding and particle size analyzing, respectively. For weighting a high precision electrical balance (Sartorious GMBH) was used. Phenol with %99.9 purity with a molecular mass of 94.11 g/mol was supplied in solid form. Samples' phenol concentration in was measured by UV-vis spectrophotometer (Optima SP-3000 Plus). In order to adjust the initial solutions' pH, H_2SO_4 and NaOH 1N were used, and for measuring pH values a digital pH meter (DHP-500, SICO, UK) was used. For evaluating the influence of ionic strength on phenol removal of $NaNO_3$, NaCl, Na_2SO_4 and $NaHCO_3$ salts were used.

2.2 Supply and Preparation of Adsorbent

Acacia tortilis pod shells was used as a natural adsorbent, was prepared as agricultural waste in the city of Iranshahr city which located at the Sistan-Baluchistan Province. In order to initially preparing the adsorbent, seeds were isolated on the pods and the pods were washed several times with distilled water to remove dust and other foreign particles. After washing for 24 h, they were dried in a hot air oven in 70°C for 3 h and stored in a desiccator. Then prepared materials as adsorbent was grinded by an electrical mill and sieved by a standard ASTM sieve with mesh size ranging from 30-60 and 60-100 and then was kept in a dry place for further use [6]. The morphologies of adsorbent were obtained by using a Field Emission Scanning Electron Microscope (FESEM, FEINova-Nano SEM-600, Netherlands) which are shown in Figure 1.

2.3 Batch Removal of Phenol using *Acacia tortilis* Pod Shells as Adsorbent

Batch experiments were carried out to investigate the effects of adsorption parameters such as pH (2-12), adsorbent dose (0.1-1.6 gr/l), adsorbent particle size (mesh between 60 - 30 and 60 -100), initial phenol concentration (0.5-64 mg/l), contact time (10-60 min) and temperature (20-45°C) for evaluating phenol adsorption by *Acacia tortilis* pod shells. The effect of ionic strength was studied by varying the concentrations of $NaNO_3$, NaCl, Na_2SO_4 and $NaHCO_3$ added individually to water solutions over the range of 0.01-0.25 M. Phenol samples were prepared daily by dissolving the appropriate amount in Deionized water and used as a stock solution (1000 mg/l) and diluted to the required initial concentration. Batch adsorption experiments were carried out in 100 ml sample flasks. To start each adsorption test, containing phenol synthetic water samples with predetermined conditions that mentioned before were loaded into a 100 ml sample flasks. For mixing and appropriate contact of the adsorbent and the adsorbate the sample flasks were shaken on a rotary shaker (GFL 137) with 120 rpm. Then, at appropriate intervals of time the amount of 25 ml of the sample was taken and filtered with filter paper (Whatman No. 45) and analyzed for the residual adsorbate (phenol) concentration by using a UV-vis spectrophotometer at wavelength of 510 nm as described in Standard Methods [10].

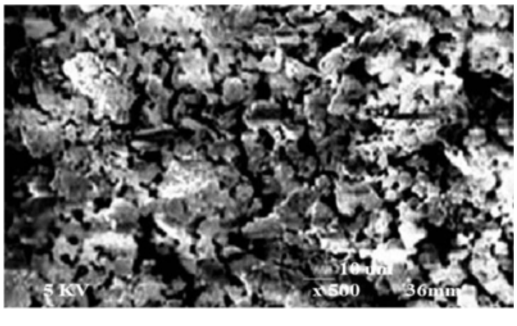

Figure 1. SEM micrograph of nanometric adsorption of *Acacia tortilis* pod shell.

In this study, the Langmuir and Freundlich adsorption isotherms were used in order to describe the relation between the pollutant and the adsorbent and were used as synthetic variables. In order to investigate the kinetics of adsorption of phenol on the adsorbent pseudo-first- order and pseudo-second-order kinetic models were used.

The amount of phenol adsorbed at the equilibrium time (q_e (mg/g)) and the efficiency of phenol removal (E) were calculated with Eq. (1) and Eq. (2) respectively [4]:

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

$$E = \frac{C_o - C}{C_o} \times 100 \quad (2)$$

Where C_0 and C_e are the initial and equilibrium concentrations of phenol (mg/l) in aqueous solution, respectively, V is the solution volume (L) and M is the mass of the adsorbent (g).

3. RESULTS

The obtained results from the experiments and chemical analysis performed onto *Acacia tortilis* pod shell are shown in Figure 2 to 13 and table 1 and 2. Results showed that the maximum efficiency of phenol removal with both 30-60 and 60-100 mesh adsorbents, can observed in pH=2 and as pH increases the amount of phenol removal decreases (Figure 2). The effect of adsorbent dose and its size in removing phenol are shown in Figure 3. As the dose of the adsorbent increases from 0.1-1.6 gr/l the amount of phenol adsorption slightly increased. Despite the fact that by increasing the dose of the adsorbent, less phenol remains in the solution, but calculations indicated that by increasing the dose of the adsorbent, the amount of the pollutant in unit of adsorbent mass decreased, therefore according to these calculations the dose of the adsorbent was determined to be 0.2 gr/l and was used for further study phases. Moreover, it was observed that as the particle sizes decreased, the quantity of phenol adsorption increased. In optimum pH, which is equal to 2, the adsorbent capacity slightly increased by increasing in contact times (from10-60 minutes) in different concentrations of phenol. Also, as the concentration of phenol increased the efficiency of removal by natural adsorbent increased too (Figsure 4-11). Temperature is another variable that was studied and presented in Figure 12. The maximum efficiency of phenol removal was achieved in 45°C which was %99.74. In Figure 13 the effect of $NaNO_3$, NaCl, Na_2SO_4 and $NaHCO_3$ in different concentrations on phenol removal with Acacia tortilis pod shells is shown. As the concentration of salts increased from 0-0.25 M, phenol removal efficiency decreased from %99.2 to %14.62, %27.15, %32.19 and %38.68 for $NaNO_3$, NaCl, Na_2SO_4 and $NaHCO_3$ salts, respectively.

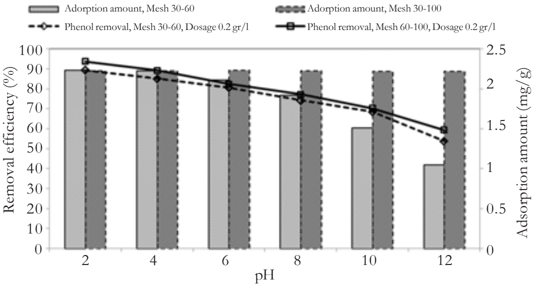

Figure 2. The effect of pH in removing phenol by using the *Acacia tortilis* pod shell and determining its optimum (initial phenol conc.: 8mgL^{-1}, Adsorbent dosage : 0.2 g L^{-1}, contact time: 30 min).

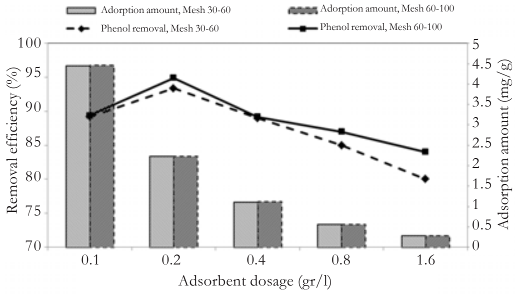

Figure 3. The effect of adsorbent dose in removing phenol by using the *Acacia tortilis* pod shell and determining its optimum (pH: 2.0, initial phenol conc.: 8mgL^{-1}, contact time: 30 min).

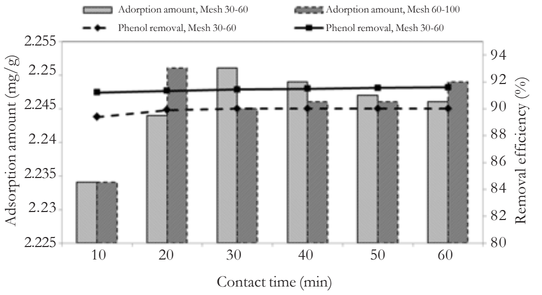

Figure 4. The efficiency of phenol removal in 0.5 mg/l concentration by using the *Acacia tortilis* pod shell adsorbent (pH: 2.0, Adsorbent dosage: 0.2 g L^{-1}).

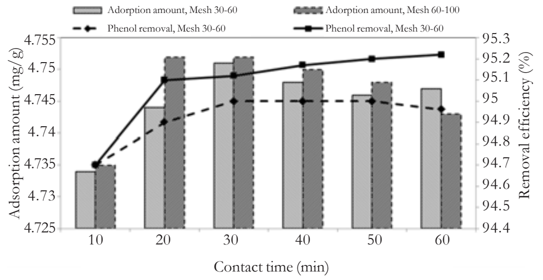

Figure 5. The efficiency of phenol removal in 1 mg/l concentration by using the *Acacia tortilis* pod shell adsorbent (pH: 2.0, Adsorbent dosage: 0.2 g L^{-1}).

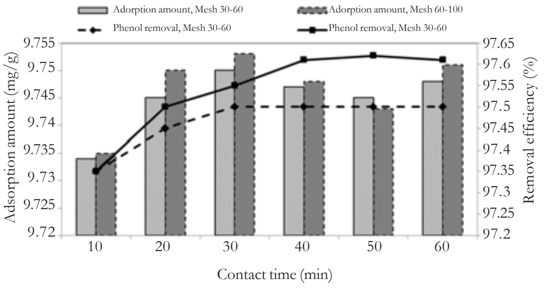

Figure 6. The efficiency of phenol removal in 2 mg/l concentration by using the *Acacia tortilis* pod shell adsorbent (pH: 2.0, Adsorbent dosage: 0.2 g L^{-1}).

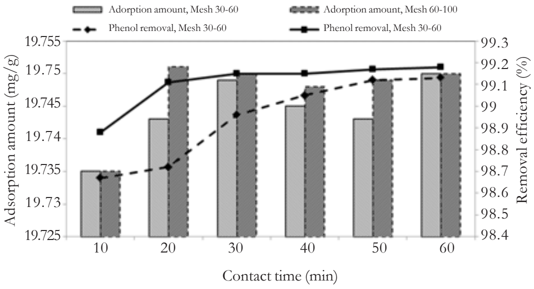

Figure 7. The efficiency of phenol removal in 4 mg/l concentration by using the *Acacia tortilis* pod shell adsorbent (pH: 2.0, Adsorbent dosage: 0.2 g L^{-1}).

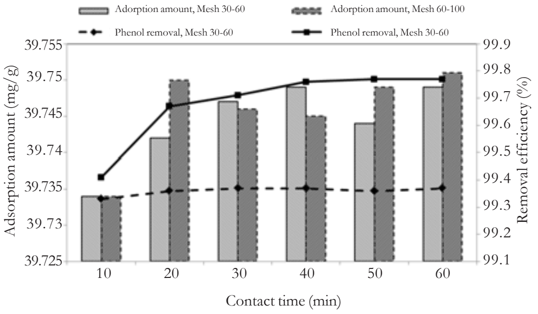

Figure 8. The efficiency of phenol removal in 8 mg/l concentration by using the *Acacia tortilis* pod shell adsorbent (pH: 2.0, Adsorbent dosage: 0.2 g L^{-1}).

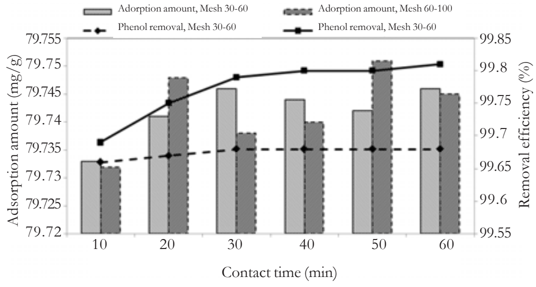

Figure 9. The efficiency of phenol removal in 16 mg/l concentration by using the *Acacia tortilis* pod shell adsorbent (pH: 2.0, Adsorbent dosage: 0.2 g L^{-1}).

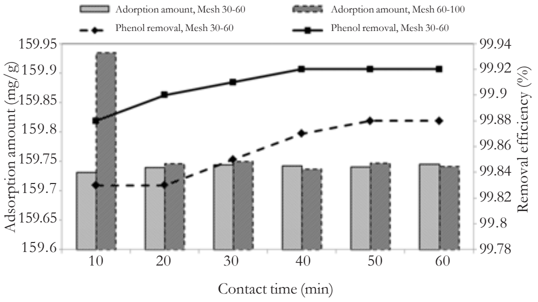

Figure 10. The efficiency of phenol removal in 32 mg/l concentration by using the *Acacia tortilis* pod shell adsorbent (pH: 2.0, Adsorbent dosage: 0.2 g L^{-1}).

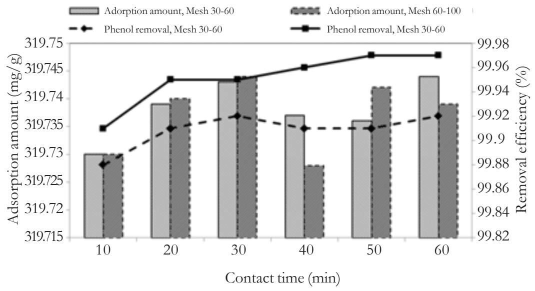

Figure 11. The efficiency of phenol removal in 64 mg/l concentration by using the *Acacia tortilis* pod shell adsorbent (pH: 2.0, Adsorbent dosage: 0.2 g L^{-1}).

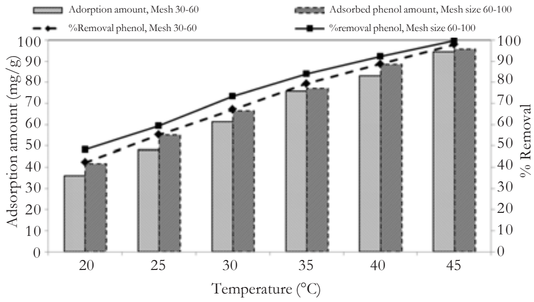

Figure 12. Effect of temperature on phenol removal by using the *Acacia tortilis* pod shell adsorbent (pH: 2.0, initial phenol conc.: 32mgL^{-1}, Adsorbent dosage: 0.2 g L^{-1}, contact time: 10 min).

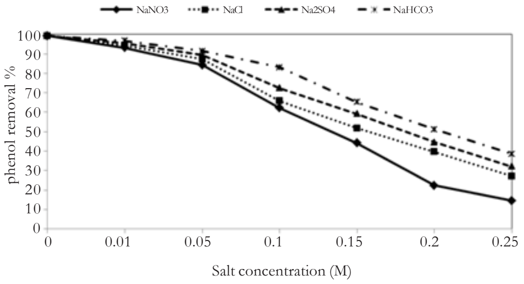

Figure 13. Effect of ionic strength on the phenol uptake (pH: 2.0, initial phenol conc.: 32mgL^{-1}, Adsorbent dosage: 0.2 g L^{-1}, Mesh size : 60-100, contact time: 10 min).

In order to evaluating the adsorbent pattern of phenol by this natural adsorbent, the Freundlich and Langmuir isotherms were used (table 1). For the same reason a solution with a 4 mg/l phenol concentration, pH of 2, contact time of 30 minutes and with different doses of adsorbents was used. Consequently, the concentration of remained phenol was measured. In order to determine the adsorbent isotherms, the linear form of these models was used. As it can be seen in table (1), the phenol adsorption phenomenon with selected adsorbent is more compatible with the Freundlich isotherm. Adsorption kinetic study indicated that the rates of sorption were found to conform to pseudo-second-order kinetics with good correlation (table (2)).

Table 1. The parameters of the Freundlich and Langmuir models.

mesh size	Langmuir isotherm			Freundlich isotherm		
	q_m(Lmg^{-1})	K_L(Lg^{-1})	R^2	K_f	n	R^2
30-60	21.32	0.31	0.88	2.46	2.57	0.93
60-100	20.18	0.27	0.82	3.75	1.99	0.86

Table 2. Parameters of pseudo-first-order and pseudo-second-order Kinetic models for the removal of phenol by *Acacia tortilis* pod shell.

$q_{e,exp}$ (mg/g)	Pseudo-first-order model			Pseudo-second-order model		
	K_1 (min^{-1})	q_{e}'$_{cal}$ (mg/g)	R^2	k_2 (g mg^{-1}min^{-1})	q_{e}'$_{cal}$ (mg/g)	R^2
8.21	-0.0165	1.86	0.7642	0. 193	8.37	0.9995

4. DISCUSSION

4.1 Effect of pH Solution

The pH is one of the important factors which can affect the adsorption process through its effect on the pollutants chemical structure and its surface electricity. Moreover, pH affects the electrical charge of adsorbents' surface according to the degree of ionization and changes the ionization degree of phenol [11,12]. As the results indicated as pH increased the removal efficiency decreased, and in pH=12 the minimum amount of phenol adsorption observed. This phenomenon is related to the effect of pH in ionization of phenol. The ionic fraction of phenol ion (φ_{ions}) is calculated from [13]: $\varphi_{ions} = 1/[1+10^{(pK_a - pH)}]$. Obviously, it was seen that φ_{ions} increased as pH increased. Therefore, phenol which is a weak acid is adsorbed in little quantities in high pH and the reason for this phenomenon is the dominant repulsive forces in high pH. Moreover, in high pH, phenol turns to salt form and is easily ionized and creates negative charge in its phenol groups and at the same time the OH$^-$ ion groups on the adsorbents prevent phenolate ions from being adsorbed [14,15]. Similar results were achieved for phenol adsorption by activated carbon from date stones in 2010 by Elnaas et al, phenol adsorption with cleap clay in 2007 by Nayak et al and phenol and chlorophil removal with modified zeolite in 2007 by Kuleyin et al [16-18].

Changing the solutions' pH is effective in the surface adsorbing process during the degradation and fragmentation of related groups on the active surfaces of the adsorbent. Therefore, this problem leads to change in the synthetics of the adsorbing phenomenon and the equilibrium characteristics between the adsorbent and the adsorbed chemical in the adsorbing process. The adsorbing of different kinds of anions and cations on these adsorbing surfaces can be explained by competing adsorption between the OH^- and H^+ ions with the adsorbed compound. Adsorbing surfaces adsorb ions better in low pH and the presence of H^+ ions. However, surfaces are activated by increasing pH and the presence of OH^- ions for adsorbing cations [16]. Phenol is a weak acid and in high pH it loses its adsorption capacity in competition with OH^- in alkaline environment, because the positive adsorbent surfaces do not have a tendency toward adsorbing phenol ions and the reason is an electro statistic repulsion. As the amount of adsorption increased, the eventual pH of the sample increased too and this is due to increase in the adsorbing surface of the $C_6H_5O^-$ phenol ion to the positive charged surfaces of the adsorbent. Because when the adsorption rate increases, phenol overcomes in competition to the OH^- ion for neutralizing the weak H^+ ions from phenol in getting adsorbed to the adsorbent and increases the presence of the OH^- ion in the solution [17, 19].

4.2 Effect of Adsorbent Dosage

Determining the optimum dose for the adsorption, due to economic reasons is another parameter which should be determined in adsorption studies, especially in big scale systems [20]. The results of this study stage showed that with increasing in the adsorbent mass from 0.1-0.2 gr/l, the amount of phenol removal increased from %70 to %90. Although with increasing in the amount of adsorbent, the concentration of the remained phenol in the solution decreased, but calculations showed that with increasing in the dose, the amount of adsorbed pollutant (in mass unit) decreased. Therefore, according to these calculations the dose of 0.2 gr/l of the adsorbent is determined and used in evaluating the other parameters. Although it is expected that increase in the dose of adsorbent leads to increase in the active surface site and increased adsorption, but the results of numerous studies have confirmed the opposite. The reason for this is that some available active parts on the surface of adsorbent remain unsaturated and lead to decrease in the adsorbing rate in mass unit [21]. Kilic et al. in 2011 reported that the reason for lack of increasing in the adsorption rate when adsorbents dose increase is that in high concentrations of the adsorbent competition between phenol which is an anion, for accessing to active surface site increases and therefore the density of adsorption increases [7]. On the other side, higher doses of the adsorbent per volume unit of water lead to overlapping in the adsorption surface and its accumulation. Therefore, the outcomes of them lead to decrease in total available surface and decrease in the pollutant adsorption rate of the pollutant, because the accumulation of adsorbents cause increases in the distribution routes during the distribution stage of the pollutant on the absorbable surfaces and consequent result is decreasing the amount of adsorption [22]. These results are in line with the results from Lin et al. in 2009 about the adsorption of phenol by resins and cheap adsorbents and Saitoh et al. in 2011 in removing phenol by chitosan attached to polymers [14, 23].

4.3 Effect of Particle Size

The effect of particle size provides important information for determining the optimum use of adsorbent and maximum amount of adsorption capacity. The synthetic of the experiment for removing phenol was by using two different 30-60 and 60-100 adsorbent meshes. The results which is presented in Figsure 4 -11 can shows that the adsorption process with smaller adsorbent particle sizes, reaches equilibrium with faster rate. When different initial concentrations of pollutant with different particle sizes are experimented, the equilibrium concentrations are different. In this study, as it can be observed the adsorbent with the 60-100 mesh has the maximum amount of adsorption capacity. For the Acacia tortilis pod shell the maximum adsorption capacity was in small pore size and when the particles of the adsorbent were smaller, more tiny holes are in contact with the adsorbing molecules and therefore diffusion occurs in faster rate. The reason for these phenomenon is that when the mass of the adsorbent remains constant, larger available external surface due to the smaller particle sizes appears. Moreover, the amount of adsorption on the solid surfaces, with available external surface for a certain amount of adsorbed mass differs with particle size and the capacity of adsorption is directly related to the total contact surface and inversely related to the particle diameter for nonporous adsorbents [23, 24]. Although Acacia tortilis with a 60-100 size gains better kinetic result, but working with smaller particles is easier, because after each experiment they get trapped in the rims of the used dishes. The results achieved in this study were in line with Roostaei et al. in 2004 study for removing phenol by surface adsorption [25].

4.4 Effect of Contact Time

In order to evaluate the effect of contact time in the efficiency of phenol removal, experiments were done during 10-60 minutes contact time. The results showed that the time required in the phenol adsorbing on *Acacia tortilis* pod shell was 10 minutes for both meshes. These results also showed that the process of phenol adsorption is a quick process, because high amounts of phenol were adsorbed by the adsorbent only in 10 minutes. As it can be seen by increase in the contact time of samples with the adsorbent, the removal rate of phenol increased and in the initial contact times, the adsorption rate is higher. The results of evaluating the effects of contact time are shown in Figsure 4-11. These results are similar to the results of some researcher and different from others. Suresh et al. in 2011 evaluated the adsorption of phenol and nitro phenol on activate granulated carbon and reported that the adsorption of phenol by the adsorbent reached equilibrium in 20 minutes [13]. But Ali et al. in 2013 evaluated alginate calcium as a biocatalyst in removing phenol and reported that 80 hours was their equilibrium time [21]. Difference in the results of this study with the results from other researchers is probably due to the different chemical structures of the adsorbents used.

4.5 Effect of Initial Phenol Concentration

The equilibrium capacity of adsorbent was evaluated in different initial concentrations of phenol. The results showed that the adsorption capacity of the adsorbent can increase with increasing in the phenol initial concentration; however the efficiency of phenol removal at the same time showed an opposite trend. This fact can be interpreted in this way that by increasing in concentration of phenol, the driving force for mass transport and therefore the speed of molecular transport from the solution toward the aqueous solution surrounding the adsorbent and eventually toward the surface of the adsorbent particles increases. On the other side, the percent of phenol removal by increasing in its initial dose decreased [14]. Increasing in the initial concentration of phenol leads to increase in the efficiency of removal and decrease in the remained concentration of phenol. This phenomenon occurs because the surface of the adsorbent has certain sites for adsorbing the pollutants and by increasing in phenol concentration in comparison to the available surface, proportionate to the number of pollutant moles that should be adsorbed, and consequently the adsorption decreased. This phenomenon leads to decrease in efficiency and increase the remained phenol concentrations in water [16]. Similar results have been reported in 2011 by Kilic et al. The researchers have reported that by increasing the concentration of phenol, the rate of its adsorption by activated carbon which derived from tobacco remaining, decreased [7]. Furthermore, Ma et al. in 2007 reached similar results in removing phenol by using artificial organo-bentonite and the reason they reported was decreasing in the proportion of adsorbing surface to the pollutant mole [1].

4.6 Effect of Temperature

The effect of temperature on phenol removal by Acacia tortilis pod shell was investigated in different solutions temperature which ranged from 20 to 45°C (Figure 12). As the temperature increased the efficiency of adsorption removal as percent increased. Maximum removal of phenol was observed at 45°C. This may be either due to the changes in the pore structure of the adsorbent. Since sorption is an exothermic process, it would be expected that an increase in temperature of the adsorbate–adsorbent system would result in decreasing the sorption capacity [26]. However, if the adsorption process is controlled by the diffusion process (intraparticle transport-pore diffusion), the sorption capacity can be increased as temperatures increased. This is due to the fact that the diffusion process is an endothermic process [27]. With increasing the temperature, the mobility of the phenol ions increased and the retarding forces acting on the diffusing ions decreased, and consequently increasing the sorption capacity of adsorbent. Increasing in phenol sorption capacity with the temperature increasing has also been reported by other investigators such as Akhtar et al. in 2006 to study about the applications of immobilized bitter gourd (*Momordica charantia*) peroxidase in the removal of phenols, Sarkar et al. in 2006 to removal of phenol and its analogues from contaminated water by using of fly ash and Kilic et al. in 2011 with the Adsorptive removal of phenol from aqueous solutions on activated carbon prepared from tobacco residues [7, 26, 27].

4.7 Effects Ionic Strength

In present study, in order to evaluate the effect of ionic strength (0.01-0.25 M concentrations) of the solution on the removal of phenol with *Acacia tortilis* pod shell, the NO_3^-, Cl^-, SO_4^{2-} and HCO_3^- ions in the form of $NaNO_3$, NaCl, Na_2SO_4 and $NaHCO_3$ were used individually and the results is shown in Figure 13. Experimental results indicate that increasing in the salt concentration resulted in reducing phenol adsorption onto *Acacia tortilis* pod shell. As the concentration of salts increased from 0 to 0.25 M, the percentage removal efficiency decreased from %99.2 to %14.62, %27.15, %32.19 and %38.68 for $NaNO_3$, NaCl, Na_2SO_4 and $NaHCO_3$ salts, respectively. The negative effect of NO_3^- and Cl^-, SO_4^{2-} and HCO_3^- could be due to the fact that the active sites of the adsorbent may be blocked in the presence of these salts and so resulted in increasing the hindrance of phenol diffusion on the surfaces of adsorbents. Moreover, the decrease in adsorption with increased ionic strength may be due to the decrease in hydrophobic nature of the dissociated phenol molecules at pH 2.0 [20, 28]. From the results, the $NaNO_3$ salt exhibited a higher inhibition of phenol adsorption compared to the NaCl, Na_2SO_4 and $NaHCO_3$salts. These results are in line with the Senturk et al. in 2009 study about removal of phenol from aqueous solutions by adsorption onto organomodified Tirebolu bentonite and Mukherjee et al. in 2007 study about removal of phenols from water environment by activated carbon, bagasse ash and wood charcoal [20, 28].

4.8 The Adsorption Isotherms

In studies on adsorbing pollutants by different adsorbents, determining adsorbing isotherms and usable adsorbing capacity is among the most important characteristics that should be considered. Analysis of adsorption isotherms in order to develop an equation to accurately display the results and for designing adsorbing systems is very important [13]. In this study, determining adsorption isotherms was done by using general Freundlich and Langmuir equations. The Freundlich model can be expressed as Eq. (3) [18]:

$$log q_e = log k_f + \frac{1}{n} log C_e \tag{3}$$

Where q_e is the amount of adsorbed phenol per mass unit of adsorbent (mg/g), K_f and n are the Freundlich constants and C_e is the concentration of the remaining phenol in the solution after reaching equilibrium (mg/l). The Langmuir model can be expressed as Eq. (4) [14]:

$$\frac{C_e}{q_e} = \frac{1}{K_f q_m} + \frac{C_e}{q_m} \tag{4}$$

Where q_m is the maximum adsorption capacity (mg/g), and K_L is a parameter which relates to the adsorption energy (L/g). Calculating the correlation coefficients (R^2) of the curves from these two adsorbing models showed that adsorption of phenol by Acacia tortilis is more compatible with the Freundlich isotherms. When $1/n=0$ the isotherm is irreversible, when $0<1/n<1$ the isotherm is favourable and when $1/n>0$, the isotherm is unfavorable [23, 29]. Because the calculated amounts for n are equal to 5 and $1/n=2$, therefore the adsorption of phenol by Acacia tortilis is compatible with the Freundlich isotherm model. The results of our study are in line with the results from Roostaei et al. in 2004 [25], but different from the results from Srivastava et al. in 2006 [15]. According to the results of this study and similar studies it can be concluded that there is no single model for adsorbing pollutants by adsorbents and the adsorbent model is dependent on the kind of pollutant and the adsorbent used [30].

4.9 Adsorption Kinetics

The Adsorption kinetics and mathematical modeling are one the most important data for understanding the uptake rates of pollutants on the surfaces of adsorbents and assessment the performance of the adsorbents [4, 30]. In order to analyze the adsorption kinetics of phenol on *Acacia tortilis* pod shell the pseudo-first-order and the pseudo-second-order kinetics models were applied to the experimental data. The pseudo-first-order equation can be written as follows [28]:

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad (5)$$

Where q_e (mg g^{-1}) and q_t (mg g^{-1}) are the amounts of phenol adsorbed at equilibrium and at time t, respectively, k_1 (min^{-1}) is the pseudo-first-order rate constant. A plot of $\ln(q_e - q_t)$ versus t gives a straight line and suggests the applicability of this kinetic model, and q_e and k_1 can be determined from the intercept and slope of the plot, respectively.

The pseudo-second-order model is in the following form [17]:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (6)$$

Where k_2 (gmg^{-1} min^{-1}) is the rate constant of the second-order equation. The plot of t/q_t versus t should give a straight line if pseudo-second-order kinetic model is applicable and qe and k_2 can be determined from slope and intercept of the plot, respectively.

The values of kinetic constants for phenol adsorption onto Acacia tortilis pod shell is presented in Table 2. According to the presented values in Table 2, the correlation coefficient (R^2) for pseudo-first-order kinetic model is relatively low which may be indicative of a weak correlation. Also, $q_{e},_{cal}$ (calculated value of solid phase concentration of adsorbate at equilibrium (mg/g)) determined from the model is not in a good agreement with the experimental value of $q_{e,exp}$ (experimental value of solid phase concentration of adsorbate at equilibrium (mg/g)). Therefore, the adsorption of phenol onto *Acacia tortilis* pod shell is not suitable for the pseudo- first-order reaction. For pseudo-second-order kinetic model, the value of correlation coefficient is strong ($R^2 > 0.99$) and the calculated $q_{e,cal}$ value is closer to the experimental $q_{e,exp}$ value. In the view of these results, the pseudo-second-order kinetic model provided a good correlation for the adsorption of phenol onto *Acacia tortilis* pod shell in contrast to the pseudo-first-order model. These results are in line with the results of Senturk et al. study in 2009 about removal of phenol from aqueous solutions by adsorption onto organomodified Tirebolubentonite, Ma et al. in 2007 about Removal of phenols from water accompanied with synthesis of organobentonite and Kuleyin in 2007 about removal of phenol and 4-chlorophenol by surfactant-modified natural zeolite [1, 17, 28].

5. CONCLUSION

Adsorption study for phenol removal from aqueous solution on *Acacia tortilis* pod shell, waste generated in the agricultural sector, was evaluated under different experimental conditions such as initial phenol concentration, contact time, dose and particle size of adsorbent and pH of solution. The obtained results demonstrated that mentioned adsorbent is capable for removing phenol effectively. It was found that the solute removal is favored at a lower solute concentration, smaller particle size of *Acacia tortilis* pod shell, lower contact time, lower adsorbent dose and at the acidic pH range. The equilibrium data is best fitted to the Freundlich isotherm model. The kinetics of phenol adsorption onto *Acacia tortilis* pod shell followed by pseudo-second-order model. Overall, the experimental results indicated that the use of *Acacia tortilis* pod shell as an adsorbent for phenol removal from aqueous solutions can be found as the cost effective way. Moreover, it can be considered as a very good adsorbent and an alternative to activated carbon and it is concluded that the *Acacia tortilis* pod shell could be exploited for commercial applications. However, future study should focus on the larger scale demonstration, comprehensive economic and environmental assessments of the proposed phenol removal technology.

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