Haloxylon Activated Carbon; a Novel Absorbent to Remove Phenol from Aqueous Solutions



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ABSTRACT

Aims Even low concentrations of phenol in industrial waste can cause many difficulties for the aquatic environment. So removal of this organic matter is an important issue. the adsorption process, is one of the most effective methods for isolation and purification of Phenols. The aim of this study was to introduce wood haloxylon as a natural and new absorbent to remove phenol from aqueous solutions.

Instrument & Methods Experiments were carried out in laboratory scale to evaluate the effect of important variables such as initial pH (4, 5, 6, 7, 8 and 9), the initial concentration of phenol (100, 50 and 150mg/l), adsorbent dosage (0.5, 1 and 2g/l) and reaction time (20, 40 and 60min). The concentration of phenol was measured by the photometric method at wavelengths of 500nm.

Findings The highest efficiency was recorded at pH=7 and at a rate of 45.2% and after it the removal efficiency dropped. The maximum adsorption of phenol happened in the first 20 minutes (35.8%) and after that, it was absorbed more slowly and took 60 minutes (45.2%) to reach the equilibrium. By increasing the concentration of phenol from 50 to 150mg/l, the removal of phenol reduced from 45.2 to 30.6% and the absorptive capacity increased of from 1.1 to 2.3mg/g. By increasing the adsorbent dosage from 0.5 to 2g/l, the removal of phenol increased from 19.1 to 45.2% and the absorptive capacity decreased from 1.9 to 1.1mg/g. **Conclusion** HTAC, in optimum conditions, can be used for pre-treatment of aqueous solution containing phenol.

Keywords Phenol; Adsorption; Activated Carbon; Haloxylon

CITATION LINKS

[1] Potential of tendu leaf refuse for phenol removal in aqueous ... [2] Technologies for the removal of phenol from fluid streams: A short review of recent ... [3] Evaluation of efficacy of advanced oxidation processes fenton, fenton-like and photo-fenton for removal of phenol from aqueous ... [4] Comparative investigation of ... [5] Removal of phenol from aqueous solutions by adsorption onto organomodified Tirebolu bentonite: equilibrium, kinetic and ... [6] Phenol adsorption onto powdered and granular activated carbon, prepared from Eucalyptus ... [7] Removal of phenol from aqueous phase by using neutralized red ... [8] Adsorption kinetics and performance of packed bed adsorber for phenol removal using activated carbon from dates' ... [9] Equilibrium, kinetic and thermodynamic studies on the adsorption of phenol onto ... [10] Adsorption characteristics of natural zeolites as solid adsorbents for phenol removal from aqueous solutions: Kinetics, mechanism, and thermodynamics ... [11] Effect of water (drought) stress on water relations of ... [12] Investigation on the properties of medium density fiberboards from mixture of saxaul and ... [13] Activated carbons from waste biomass by sulfuric acid activation and their use on ... [14] Preparation of activated carbon from a renewable bio-plant of Euphorbia rigida by H2SO4 activation and its adsorption behavior in aqueous ... [15] Standard methods for the examination of water and ... [16] Individual and competitive adsorption of phenol and nickel onto multiwalled carbon ... [17] Adsorption of phenol from aqueous solutions using mesoporous carbon prepared by two-stage ... [18] Removal of phenol from petroleum refinery wastewater through adsorption on date-pit activated ... [19] Removal of cyanide from water and wastewater using granular activated ... [20] Adsorption of phenol from aqueous solutions by Luffa cylindrica fibers: Kinetics, isotherm and thermodynamic ... [21] Simultaneous co-adsorptive removal of phenol and cyanide from binary solution using granular activated ... [22] Adsorptive removal of phenol from aqueous solutions on ... [23] Palm shell activated carbon impregnated with task-specific ionic-liquids as a novel adsorbent for the ... [24] Adsorption of phenol with modified rectorite from aqueous ... [25] Application of a chemically modified green macro alga as ... [26] Phenol removal from aqueous ... [27] The application of activated carbon produced from ...

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Introduction

Phenol (C₆H₅OH) and phenolic compounds are organic pollutants that were found in industrial effluent. Industrial wastewater from pulp and paper, resin, coal, tannery, textile, plastics, rubber, pharmaceutics, and oil industries contains different types of phenolic compounds [1]. The presence of phenol in wastewater, industrial even at low concentrations, creates many difficulties for the aquatic environment. Phenol is quickly absorbed through the skin and eyes upon contact and exposure to it can result in coma, seizures, and cyanosis even though death [2]. Therefore, the removal of phenol and reducing its concentration to permissible levels before discharging to environment is necessary.

There are several advanced methods to remove phenolic compounds from wastewater, e.g. electrochemical oxidation, chemical coagulation, photo-catalytic degradation, bioremediation. membrane separation, adsorption, and solvent extraction ^[3]. High costs, low efficiency and production of toxic byproducts are limiting factors for many applications of the above methods ^[4]. Among these, the adsorption is the most powerful phenol removal method. This method has significant advantages; high efficiency, easy operation, high selectivity, low operating costs, comfortable regeneration that minimize chemical or biological sludge production.

Phenol adsorption on activated carbon is a well-known process that has high absorptive capacity due to large surface area of activated carbon ^[5]. Other adsorbents, e.g. eucalyptus wood ^[6] neutralized red mud ^[7], dates' stones ^[8], chitin ^[9] and zeolite ^[10] have also been studied instead activated carbon. Haloxylon is one of the dominant desert halophile plants species that exist in abundance in Iran, and grow in areas with an annual rainfall of less than 200ml, such as Kashan, Qom, Kerman and several other areas in Iran and many regions in other countries ^[11]. Due to the long life, physiological features, and the necessity of pruning and thinning trees, a considerable amount of haloxylon wood is produced each vear [12].

The aim of this study was to evaluate the power of haloxylon tree activated carbon (HTAC), as a natural absorbent, to remove phenol from aqueous solutions.

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HY: 30.00 k// WD: 8.1579 mm VEGAN TESCAN MAG: 34 x Det: SE 1 mm field: 4.21 mm Pc: 10 Performance in nanospace





Viewfield: 144.5 µm PC: 16 Performance in nanospace **Figure 1)** SEM images of the activated carbon particles at different magnifications

Instrument & Methods

After collecting and crushing, haloxylon tree wood were completely washed with water and rinsed with distilled water. 200g of wood chips was poured into a container with 200ml of concentrated sulfuric acid (98%) with a ratio of 1 to 1 and thoroughly stirred and allowed to be exposed to each other for 24 hours and dried for 24h at 110°C. Finally, samples were burned in the furnace at 600°C temperature for an hour, and then the furnace was turned off and allowed to be cooled and reached to the ambient temperature. Obtained HTAC was washed several times with distilled water and then soaked in a solution of 1% sodium bicarbonate (NaHCO₃) to remove and neutralize any remaining acid. The samples were washed with double distilled water until the pH was adhered between 6 and 7 and then dried at 120°C for 24 hours. The prepared HTAC was crushed with a porcelain mortar and grading by a sieve of 18 and 60 mesh with a diameter between 0.25 to 1mm [13, 14]. The outer surface of activated carbon particles of haloxylon tree contain gaps and pores. The size distribution of the most of particle (73.3%) were between 0.5 to 1mm (Figure 1).

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Double distilled water was used to prepare the synthetic solution and all reagents. Phenol stock solution was prepared by dissolving 1g of phenol (purity greater than 98%) in a liter of double distilled water. For plotting of standard curve, first 5 standard samples with concentrations of 1, 2, 3, 4 and 5 mg/l was prepared and their absorption were measured using a spectrophotometer model DR/2010 (HACH; USA) and the reaction of phenol was analyzed with 4-Aminoantipyrine at 500nm and a standard curve was plotted [15]. Optimum pH was determined of 4, 5, 6, 7, 8 and 9 in the initial phenol concentration of 50mg/l, adsorbent dose of 2g/l and contact time of 60 minutes. This study was conducted in 3 concentrations of phenol (50, 100 and 150mg/l), 3 adsorbent dosage (0.5, 1 and 2g/l) and 3 detention time (20, 40 and 60min). Triplicate for each sample was taken and average results were presented.



Figure 2) Effect of pH (a), contact time (b), initial phenol concentration (c) and adsorbent dose (d) on adsorption of phenol by HTAC (initial phenol concentration of 50mg/l, adsorbent dosage 2g/l, contact time 60 minutes and pH=7)

Phenol removal rate was calculated for each sample according to C_i - C_f/C_i where C_i was initial concentration of absorb ate and C_f was final concentration of adsorbate in terms of mg/l. Absorption capacity (q_e) was calculated by (C_i - C_f)v/w where q_e was adsorption capacity (mg/g), v was the volume of the solution adsorbate (l) and w was the adsorbent (g).



models for phenol adsorption on HTAC

Findings

Increasing the pH from 4 to 6, increased the removal efficiency from 20.5 to 43.2%. The highest efficiency was recorded at pH=7 and at a rate of 45.2% and after it the removal efficiency dropped (Figure 2a). The maximum adsorption of phenol happened in the first 20 minutes (35.8%) and after that, it was absorbed more slowly and took 60 minutes (45.2%) to reach the equilibrium (Figure 2b). The absorption was strongly dependent on the initial concentrations of phenol, in a way that by increasing the concentration of phenol reduced from 45.2 to 30.6% and the absorptive capacity increased of from 1.1 to

2.3mg/g (Figure 2c). By increasing the adsorbent dosage from 0.5 to 2g/l, the removal of phenol increased from 19.1 to 45.2% and the absorptive capacity decreased from 1.9 to 1.1mg/g (Figure 2d).

Comparing R^2 parameter of Langmuir (0.9096) and Freundlich (0.9885) isotherm models indicated a high correlated coefficient between the obtained results of HTAC for phenol removal from aqueous solutions (Figure 3).

Discussion

In this study the activated carbon made of Haloxylon tree by chemical activation, using H_2SO_4 as activation agent, was used as a natural adsorbent. The maximum removal of phenol was obtained at pH=7 and in pH higher and lower than 7, the removal efficiency was dropped. Abdel-Ghani et al. have found similar findings in a study for phenol removal on carbon nanotubes ^[16]. pH solution has reported the most effective parameter on absorbent surface charge and ionization [17]. In low pH, the presence of H+ ions and their absorption on the location of carbonyl ionization suppress phenol and decrease phenol absorption on the polar adsorbent. In high levels of pH, phenols are as salt form and easily ionized and carry a negative charge to phenolic groups and causes the increase of OH- functional groups that prevent absorption of phenol on the adsorbent ^[18,19]. Abdelwahab & Amin study on removal of phenol by Luffa cylindrica fibers have reported pH=7 as the optimum pH ^[20].

Contact time is one of the most important parameters to determine the equilibrium time of adsorption process. The highest phenol absorption occurred in the first 20 minutes and after that, it was absorbed more slowly and took 60 minutes to reach the equilibrium. In physical adsorption, more absorbable species are absorbed in a short time span but strong chemical bonds requires a long contact time to achieve a balance [21]. On the other hand, high absorption of the phenol at the start of testing is due to high absorption sites and phenol ions can be absorbed easily in these sites. As the time passing by, the number of active sites on the surface of the absorbent decreases and remained empty places on the adsorbent surface due to the repulsive forces between molecules of phenol in solid phase and liquid phase, so the removal rate is reduced ^[5]. Kilic *et al.* have reported similar results in a study of the adsorption of phenol on tobacco residues and the maximum removal rate was reported in 60min contact time [22].

The absorption was strongly dependent on the initial concentrations, so that by increasing the initial concentration of phenol, removal rate decreased. At low the concentration of phenol, the number of active sites attract more than the number of molecules of phenol and phenol molecules can easily occupy them. However, at high concentrations of phenol the number of active sites occupied by phenol molecules is not sufficient ^[19]. On the other hand, our findings were indicated that the adsorption capacity with increasing increased the initial concentration of phenol. The reason for this can be attributed to that with increasing the initial concentration of phenol in a fixed adsorbent dosage, the mass transfer rate or the penetration rate of phenol on the existing place of adsorbent is increased, thus resulting in the increasing absorptive capacity of the adsorbent ^[5]. In addition, increasing the absorption capacity by increasing the initial concentration of phenol can be due to an increased risk of collisions between ions and adsorbent particles [18]. Tor et al. have found similar results in a study for the adsorption of phenol on neutralized red mud [7].

By increasing the dose of adsorbents, the removal of phenol increased and phenol adsorption capacity decreased. The reason of phenol increasing by increasing the adsorbent dose is further increasing of active and effective surface area of adsorbent [23]. On the other hand, absorption capacity reduction with increasing adsorbent dosage can be attributed to remained unsaturated absorbing locations during the absorption reaction [24]. The most important factor is that in high doses of absorbent, the phenol molecules are insufficient to cover all exchange locations on the adsorbent, thereby reducing absorption capacity [25]. Bazrafshan et al. have found similar results in a study on removal of phenol by ash pistachio shells ^[26].

By applying Freundlich model, the value of K_f was 513.6887, which indicated phenol's easy adsorption on Haloxylon tree's activated carbon with a high adsorption capacity.

n=1.96 and 1/n=0.51 indicated phenol's optimal adsorption on Haloxylon tree's activated ^[19]. Phenol adsorption on HTAC following Freundlich isotherm model may be related to heterogeneous distribution of active places on HTAC [22]. The results also indicated that the surface of HTAC, have а heterogeneous distribution and phenol multilayer covering has happened on the adsorbent surface. This means, that adsorption process has been heterogeneous and multilayer ^[27]. R_L value was equal to 0.5784, which was more than zero and less than 1 and this indicates the phenol optimal adsorption on HTAC.

Conclusion

The maximum efficiency removal of phenol was occurred at pH=7, contact time of 60 minutes, initial concentration of phenol 50mg/l and adsorbent dosage of 2g/l. In these circumstances, phenol removal by HTAC is 45.2%. HTAC, in optimum conditions, can be used for pre-treatment of aqueous solution containing phenol.

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