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ARTICLE

PHENOL ADSORPTIVE BY CUMIN STRAW ASH FROM AQUEOUS ENVIRONMENTS

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ABSTRACT

Due to the increasing use of the adsorption process for the removal of environmental pollutants, selecting a suitable material as an adsorbent has been a major concern of researchers in this field from the technical and economic aspects. This study aims at identifying the possibility of using Cumin Straw Ash (CSA) for removing phenol from aqueous solutions. Cumin Straw Ash was used as an adsorbent at a rate of 2.4, 8.15 and 25 mg/l in laboratory scale in a batch system and changes of phenol concentration, pH and contact time and the adsorption process abeyance from Freundlich and Langmuir equations was investigated. All experiments were performed according to Examination of Water and Wastewater Standard Methods. Besides, Excel software was used to analyze the data and Cumin Straw Ash is highly efficient in removing phenol and the absorbed phenol is reduced by increasing the pH value and removal efficiency is directly related with the increase of adsorbent. The best adsorption efficiency was obtained with adsorbent dosage (dose) of 0.1 g/100 ml, pH 7, phenol concentration 10 mg/l and the contact time of 75 min. Moreover, phenol adsorption process on Cumin Straw Ash obeys from Freundlich isotherm more than Langmuir isotherm. Low cost of cumin straw and the use of Cumin Straw Ash in phenol removal are recommended as an alternative or an option together with other treatment methods.

KEY WORDS
Phenol, Adsorption, Cumin Straw Ash, Aqueous Environments

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INTRODUCTION

Phenol (C_6H_6O) is a cyclic hydrocarbon with a molecular weight of 94.11 g/mole and is a bisphenol or white solid in special case. Phenolic compounds are hydrocarbons that hydroxyl group has formed bonds with carbon atoms of benzene ring in their molecular structure [1]. Normally, the phenol is produced from coal tar and gasoline distillation and artificially by heating sodium sulfate benzene with aquatic soda at high pressure [2]. Contamination of water by phenol is considered as one of the most important environmental issues with high toxicity and is found in agricultural wastewaters due to use of some pesticides, industrial wastewater such as pharmaceuticals as well as paint and petrochemical industries and coal-fired power plants. Some of the main pollutants considered as phenol containing sources are chemical industrial wastewater applied in the manufacture of resins, plastics, fibers, adhesives, iron, steel, aluminum, lead and detergents. Moreover, these sources have been found in disinfectants, detergents, cigarettes and vehicles exhaust and are used in the preparation of household products, biocides and dyes [3-7]. In addition to synthetic ways, phenol goes into water resources through the natural ways and also because of the physical structure found in most chemical compounds, it can also be found in municipal wastewaters and is particularly concerning due to environmental stability, solubility in water and health problems. Very high concentrations of phenol, if ingested, inhaled or absorbed through the skin can cause death [8]. In addition to health risks, this material is important due to taste and smell. One consequence of phenolic compounds is the creation of chlorophenol compounds during chlorination of drinking water which leads to objectionable stench by consumers. Moreover, phenol risks and its derivatives can cause several health problems. Therefore, phenol has been classified as a pollutant with particular and hazardous priority [9 , 10]. World Health Organization (WHO) Guidelines for the concentration of phenols, chlorophenol and 2,3,4,6-tetrachlorophenol recommends the level of 0.1 µg/l in drinking water (0.1ppb). According to the US Environmental Protection Agency (U.S EPA), the permitted level of phenol in water resources of human communities and the water used for fish breeding are 0.3 and 2.6 mg/l respectively

[9]. Due to these problems, removing these types of organic compounds from chemical and petrochemical industrial wastewater is one of the necessary components in Wastewater Treatment Systems of these industries. Several different physicochemical methods are used in this method to remove phenol and phenolic compounds from aqueous solutions as follows: Distillation with steam, chemical oxidation with hydrogen peroxide, deposition, ion exchange, electrochemical methods, irradiation, activated carbon and volatile ash. However, the absorption process is one of the efficient and effective techniques [1, 3, 9-11]. but the adsorption process is an efficient and effective technique (2, 8, 11). Since activated carbons have high adsorption capacity, they are widely used as an adsorbent for organic contaminants. Activated carbon adsorption ability is related to the high surface to volume ratio and pores size. In addition, activated carbon adsorption capacity depends on the activation method and the activated carbon source. Silica and activated Alumina are used as adsorbents [12]. The use of activated carbon to remove chlorine, separating the gases and air pollution treatment, recycling heavy metals and food industries and removal of potentially polluting substances such as phenol and phenolic derivatives from aqueous solutions have many applications. But due to high cost, other options have been suggested as an alternative. The use of ash as a low-cost adsorbent is recommended for the removal of phenolic compounds. Ash is a viable alternative to activated carbon due to the low cost of it [13-18]. Ash can be produced from a wide range of carbonous materials such as wood, coal, walnut shell, fruits core, agricultural wastes, etc [14]. Cumin straw is one of cheap and available agricultural wastes in the country and it can be used as a low-cost and even free adsorbent for the removal of phenol and phenolic compounds. It is because Iran is the largest producer and exporter of cumin straw contributed about 40% of world production, and cumin straw is generated in many parts of the country (Khorasan, Semnan, Isfahan, Yazd, Kerman, Tabriz) (19).Due to high production of agricultural wastes, it was decided to test cumin straw as a cheap and available agricultural waste material.

MATERIALS AND METHODS

At first Cumin Strawcollected from farms were well washed with distilled water several times. After drying at 700 °C, they were placed inside the furnace for 120 minutes and the generated ash was sifted with the help of standard mesh sieves of 20 and 100 after crushing with porcelain mortar to obtain ash grains with a diameter ranging from 0.15- 0.85 mm. Then it was held in the desiccator to prevent moisture absorption. To provide the stoke sample contaminated with phenol, the solid phenol produced by Merck Company of Germany with 99.9% purity and the molecular mass of 94.11 was used [4]. 1000mg of this phenol is weighed and moved into a 1000ml volumetric flask and while mixing with distilled water, it was brought to the desired volume and 2 mL of sulfuric acid (1 N) was added to it. (This solution remains stable at refrigerator temperature of 4 °C for 28 days) (20). In order to determine the pH effect of samples on the adsorption process using H_2SO_4 and NaOH (0.1 N), the pH was set in the range of 2-12 using pH meter (Ultra Basic UB-10). To determine the effect of adsorbent dosage on the adsorption process, the doses of 2.4, 8.15, 25 mg/l were used and to determine the effect of absorbent contact time, 10, 20, 40, 60, 90, 120, 150 and 180 minutes were applied.To investigate the effect of the phenol concentration in the removal process, the concentrations of 5, 10, 20, 40 and 80 mg/liter were used (To create optimal conditions of contact, a shaker with a speed of 150 rpm was used). After the elapse of contact time in the adsorption process, the sample was passed through the Whatman filter and measured by colorimetric method with the 4- aminoantipirin reagent using spectrophotometer (model PD-303 UV) at the wavelength of 500 nm according to Method 8047 [21]. After obtaining the results using the software Excel 2010, the curves were plotted and the peak and optimal points were determined and reported in accordance with testing conditions.

RESULTS

The results of this study about the effect of pH in aqueous solution in the removal efficiency of phenol by Cumin Straw Ash, the effects of contact time and the adsorbent dosage on the performance of system for the removal of phenol and finally Freundlich and Langmuir adsorption isotherms for the adsorption used in this research, are represented in [ig.1 to 6] in this research.

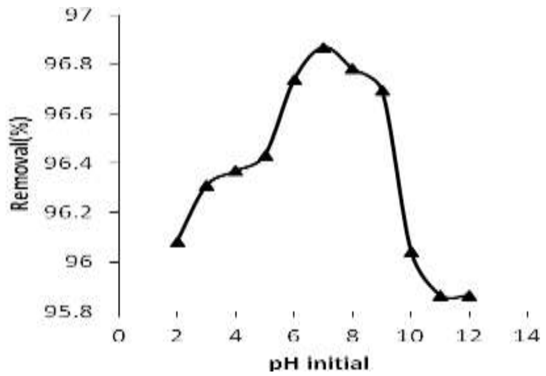

Fig. 1: The effect of pH on the adsorption of phenol on the Cumin Straw Ash
(Initial phenol concentration: 50 mg / l, adsorbent dosage: 0.03 gr/100l, contact time: 60 min)

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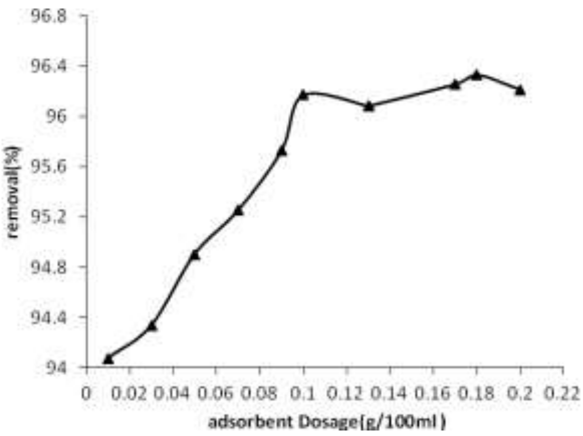

Fig. 2: The effect of adsorbent dosage on the adsorption of phenol on the Cumin Straw Ash (phenol concentration: 50 mg/l, optimum pH: 7 and contact time: 60 min).

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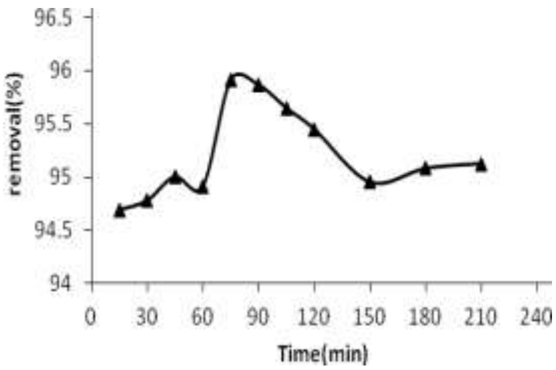

Fig. 3: The effect of contact time on the adsorption of phenol on the Cumin Straw Ash (phenol concentration: 50 mg/l, optimized pH: 7 and the optimized adsorbent dosage: 0.1 g/100 ml).

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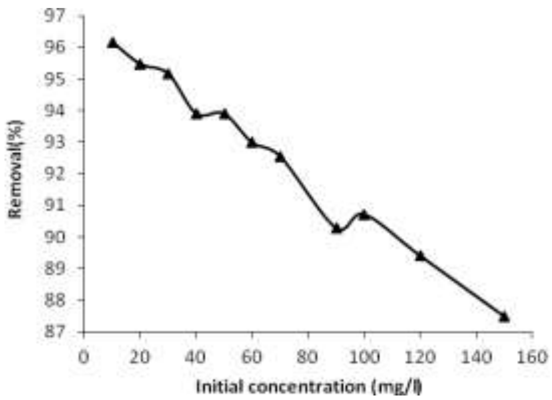

Fig. 4: The effect of phenol concentration on the adsorption of phenol on the Cumin Straw Ash (optimized adsorbent dosage: 0.1 g/100 ml, optimal pH: 7, optimal contact time: 75 min).

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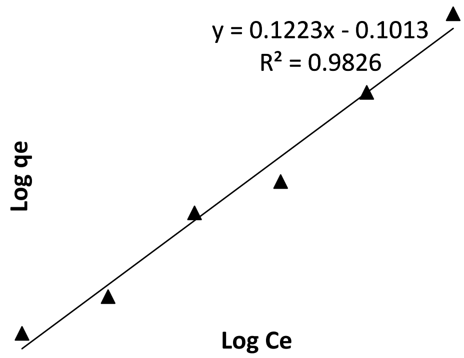

Fig. 5: Linear isotherm of Freundlich adsorption for phenol by CSA at a temperature of 23 °C.

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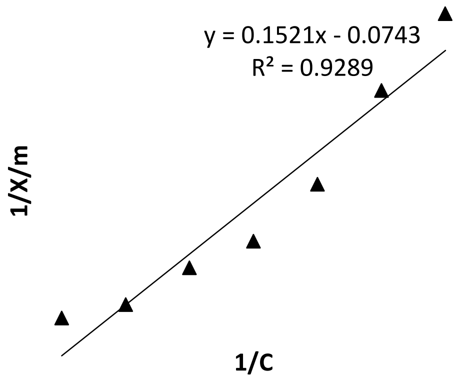

Fig. 6: Langmuir linear isotherm for adsorption of phenol by CSA at 23 °C.

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The effect of initial pH

The adsorption of phenol from aqueous solution is completely dependent on the pH of the solution because pH affects the electrical charge quality of adsorbent surface and changes the ionization degree of the phenol (22). The results of pH effect on adsorption process are represented in Figure [1] and, as expected, the amount of adsorbed phenol decreases by increasing the pH. This phenomenon is related to the effect of pH on phenol ionization. Phenol which is a weak acid (PKa 10) will be slightly adsorbed at high pH due to dominant repulsive forces. Phenol is also in the form of salt at high pH and will be easily ionized and creates negative charge in phenolic groups and the OH ionic groups on the adsorbent prevent from phenolate ions absorption at the same time [20]. In this regard, similar results are provided for the adsorption of phenol on palm kernel by Rengaraj and bentonite by Banat [23, 24].

The effect of adsorbent dosage

The effect of adsorbent dosage on the adsorption process efficiency is represented in Figure [2] and the values of 0.01- 0.2 g/100 ml have been considered in this regard. The results show the efficiency of 96% for samples with phenol concentrations of 50 mg/l. This is due to the special features of Cumin Straw Ash in terms ofcarbon content due to the burning of organic matters in Cumin Straw and increasing the active surface and porosity on the ash surface.

The effect of contact time

To evaluate the effect of contact time on the efficiency of phenol removal process, the samples with initial concentration of 50 mg/l and the absorbent with concentration of 0.1 g/100 ml were prepared. The results showed that the time required for achieving high efficiency (95.90%) in the adsorption process of phenol on Cumin Straw Ash is 75 minutes.

The effect of initial phenol concentration

Exchange capacities of sorbent adsorption (Cumin Straw Ash) in different concentrations of phenol are provided in Figure 4. According to the results of the initial concentration effect of phenol in Figure 4, it was observed that the efficiency of absorption decreases with increasing concentration of phenol. It seems that with increasing the concentration of phenol, adsorption capacity of the adsorbent rises which may result in an increase in the mass transfer force and thus increasing the absorption capacity (23, 24). This is consistent with Daraei's study for phenol adsorption on Ostrich Feathers Ash (25).

The phenol adsorption isotherm (Langmuir and Freundlich)

Adsorption Isotherm: Adsorption isotherms are equilibrium data used to explain the interaction between adsorbed and absorbent materials. Isotherms are also expressing absorptive capacity of an adsorbent. In the present study, to evaluate the empirical data analysis and describing the absorption equilibrium in adsorption between solid and liquid phases, Langmuir and Freundlich models were used. The obedience of each model is determined with plotting the curve of each balance and investigating the Correlation Coefficient of model (R^2) with experimental results (26).

Langmuir isotherm: Langmuir isotherm model is based on scientific assumptions the most important of which is that adsorbed materials (atoms, molecules or ions) are bond to identical spots on the surface of the adsorbent and monolayer adsorption process occurs. These assumptions also express that all places of adsorption have the same consistency to the adsorbed material molecules and no transition happens from the adsorbed material at the adsorbent surface (26, 27), and this is presented by the following equation [1]:

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

In this equation, qe is the amount of adsorbed phenol per a certain amount of consumed adsorbent and C_e (mg/L) is the solution equilibrium concentration and q_m is the maximum phenol required for the formation of two layers (mg/g). At the same time, Langmuir equation can be drawn linearly to determine the Langmuir adsorption constants (K_L) and maximum adsorption capacity of the adsorbent (qm). The values of qm and K_L can be achieved by charting 1 / q vs. 1 / Ce.

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

Freundlich isotherm is merely an experimental model based on adsorption on heterogeneous adsorbent surface which is described by the following equation [3]:

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

In this equation k_f and 1/n are Freundlich adsorption constants related to the capacity and absorption rate. Freundlich equilibrium constants are obtained by charting ln qe against ln Ce based on empirical data of intercept as K_f and slope as 1/n. Freundlich equation can be linearized for determining Freundlich adsorption constants as follows (28-29). equation [4]:

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

According to the results observed in the Graph (5, 6), the phenol adsorption on Cumin Straw Ash properly functions from Freundlich isotherm. Freundlich model presents a more reliable description physically for absorbing contaminants on organic materials and this can be due to the presence of different absorption bands on organic materials.

CONCLUSION

Phenol pollution has dangerous special priority with known or carcinogenic-suspected harmful effects, mutagenic effects, and severe damages to the fetus or detoxification. Considering the results of this study, Cumin Straw Ashcan be effectively and efficiently being used for the removal of phenol in aqueous solutions. Phenol removal percentage is a function of initial phenol concentration, contact time, pH and adsorbent dosage.This adsorbent is able to remove about 95.99% of phenol from solutions with initial concentration of phenol as 10 mg/L.The adsorption on the Cumin Straw Ashwas described by Langmuir and Freundlich adsorption isotherms, which indicates better performance of Freundlich adsorption isotherm with data obtained from this study. The removal of phenol from aqueous solutions at low concentrations of phenol is influenced by adsorption on solid adsorbent surface sites, while This is despite the fact that adsorption occurs at the surface and internal exchange of both of them. Finally, it is concluded based on the results obtained from the present study that Cumin Straw Ash has high capacity in adsorbing phenol from aqueous solutions and thus it can be used as a practical strategy for removal process from wastewater of industries that use phenol.

CONFLICT OF INTEREST
There is no conflict of interest.

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FINANCIAL DISCLOSURE
None

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