

Original Article

Phenol Removal from Aqueous Solutions by Adsorption on Activated Carbon of Miswak's Root Treated with $KMnO_4$ Hamed Biglari¹ Mojtaba Afsharnia¹ Nasibeh Javan² *Seyed Ali Sajadi¹

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Abstract

Background and Purpose: Phenol and derivatives are common pollutants of drinking water which are blamed for crucial adverse effects such as poisoning, cancer, and malformation. In this study, an activated carbon of Miswak's root (MR) was used for the removal of phenol from aqueous solutions as a low-cost and high surface adsorbent.

Materials and Methods: Adsorption experiments were then conducted in a batch reactor with activated carbon prepared from MR and treated with $KMnO_4$ to study the effects of contact time (0-180 minutes), pH (3-13), initial phenol concentration (100-1000 mg/L), and adsorbent dosage (0.1-1 g/L) at lab temperature $30 \pm 1^\circ C$ on sorption efficiency. $KMnO_4$ treatment influenced the physicochemical properties of the carbon and improved its adsorption rate.

Results: The results showed that the equilibrium time of adsorption was 120 minutes maximum adsorption capacity (94.76% phenol removed) of the MR carbon was 142.15 mg/g at pH 5, the initial concentration of 100 mg/L, $30^\circ C$ and 180 minutes contact time. The optimum type of MR adsorbent was produced in $800^\circ C$. The equilibrium data were analyzed by the Langmuir and Freundlich isotherms and fitted well with the Freundlich model ($R^2 = 0.9821$) better than Langmuir ($R^2 = 0.7551$) model.

Conclusion: The results revealed that the carbon of MR modified with $KMnO_4$ had a satisfactory quality in phenol adsorption and can well be used as a novel, inexpensive, effective, and efficient adsorbent for the removal of phenol from the aquatic environment.

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Key words: *Salvadora Persica*, Miswak's Root, Adsorption, Freundlich, Phenol

1. Introduction

The contamination of water sources with organic and inorganic pollutants has been being the most important concern in water treatment plants (1-3). Of all organic matter, phenol derivative compounds are among the most common contaminants that make water non-drinkable, even in very low levels (4-7). Phenol intruding water bodies as a result of natural processes and human activities is a considerable concern due to its persistency, unpleasant taste and odor, solubility, carcinogenic, toxicity, mutagenic and malformation effects, poor biodegradability and accumulation potential in plants and tissues (i.e., fish living in lakes and rivers contaminated with phenolic compounds have a queer taste and bad odor) (3,8-11). The US Environmental Protection Agency listed phenolic compounds as priority pollutants with a discharge limit to water bodies of < 1 mg/L in the treated effluent to protect human health from the potential toxic effects caused by exposure to phenol (12). Furthermore, according to the World Health Organization regulation recommended 0.001 mg/L as the permissible limit for phenol concentration in potable water. In Iran, a maximum phenol level of 1.0 mg/L is permitted in wastewater for discharge to surface water resources by the Institute of Standard and Industrial Research of Iran (13). There are various methods for removing phenol from aquatic solutions such as adsorption, aerobic and anaerobic biological processes (14), oxidization by ozone, and ion exchange through resins (15).

One of the most effective techniques for removing organic pollutants from water is using carbon as an adsorbent (16). Synthetic activated carbon can remove a verity of pollutants from water and wastewater; however, it is an expensive substance that increases treatment costs (17,18). Therefore, needs for economical alternatives led to widespread researches to find a practical, effective, and reasonable technique (19,20).

Salvadora Persica, known as Miswak plant is an evergreen small tree with light green straggling and drooping branches. Miswak is widespread naturally grows in most parts of Africa, India, Jordan, Oman, Pakistan, Saudi Arabia, and in the south of Iran. It is called Chooj in the south of Iran, Shajar-olmiswak in Arabic, and Arak in the olden Persian texts (21). Considering its medicinal uses, nowadays, Persica is cultivated around the world, including Iran (22). Since there is a considerable amount of wastes after extracting pharmaceutical components, they could be considered as adsorbent (23).

Phenol removal within adsorption has been investigated in many studies. A study completed in 2011 examined vegetal cords found 6.21 mg/L removal of phenol by 1 g of adsorbent in wastewater samples (24). Moreover, in another study in 2011, phenol removal by carbonized wheat chaff and pinewood sawdust was found to be 83.88 and 39.30 mg/g, respectively (25). Din et al. (2009) examined the batch adsorption of phenol within physiochemical-activated coconut shell. They achieved decrease of 205.8 mg/L phenol per 1 g adsorbent (26). In another study, phenol removal from aqueous solution by the ash of avocado kernel seeds was investigated. Phenol concentration decreased 70% while the initial level was 500 mg m⁻³ (27). Accordingly, this study was conducted to evaluate the capacity of carbon of Miswak's root (MR) modified with KMnO₄ in the removal of phenol in an aqueous environment.

2. Materials and Methods

2.1. Preparation of materials

This was an experimental study conducted in a laboratory scale. All chemicals used in the experiment were supplied by internationally approved companies. To assure the material quality and prevent any contamination, they were kept in a bottle cooler. MR was obtained from natural habitat in Zahedan, in the south of Iran, was used as a precursor for the

production of activated carbons by H_3PO_4 activation and KMnO_4 treatment.

The roots were washed with tap water to remove any mud and other impurities. Then, they were rinsed with distilled water for few times and dried in an oven under the temperature of 105°C for 1 hour, crushed, and finally ground in a laboratory mill (25). Then, the material was immersed in 40 wt. % phosphoric acid solutions at a ratio of 1:2.5 (MR: H_3PO_4 , w/w). After soaking overnight at lab temperature, the wet mass was transferred to a muffle furnace and activated at 300°C , 400°C , and 800°C for 1 hour. Then, the product was cooled to lab temperature and washed with distilled water until its filtrate reached neutral pH. The resulting activated carbon material was dried at 120°C for 2 hours, ground, and sieved in an American Standard Test Sieve Series mesh. The size of granules for experiments was selected to be 0.15-0.85 mm before placing in a desiccator (28).

KMnO_4 treatment of activated carbon was carried out by dipping and heating methods. MR was put into 10^{-3}M KMnO_4 solution, 5:1 (w/v, g/L) for 22 hours at lab temperature. Then, the solvent was totally removed, and a black compound was obtained. The compound was further dried at 100°C for 1 hour and 150°C for 0.5 hour and heated at 300°C for 1 hour in a muffle furnace. After treatment, the sample was cooled to lab temperature and stored in the desiccator (28).

2.2. Experimental procedure

At first to the procedure, the experiments sample was prepared by dissolving the required amount of original stock solution of phenol dissolved 1 g in 1000 ml distilled water. The solution with the preliminary

concentration of 100 mg/L was used for the experiment (Table 1). To achieve the optimum mode, a variety of pH was exploited. The initial pH (3-12) of the solution was adjusted by a 0.1 N NaOH or H_2SO_4 . A portable Denver Ultra basic-UB10 Model pH meter was used for measuring pH values in the aqueous phase.

To find the appropriate adsorption isotherm, the experiment was conducted by varying the adsorbent dosage from 0.1 to 1 g/L for 1000 ml of samples. After that, the samples were mixed in incubator equipped bottle shaker under 150 rpm (for constant temperature, $30 \pm 1^\circ\text{C}$) to reach equilibrium. All experiments were performed under the temperature of $30 \pm 1^\circ\text{C}$; with various contact times: 10, 30, 60, 80, 100, 120, and 180 minutes. The whole procedure was repeated twice to guarantee precision and accuracy (11,27). Finally, by centrifuging under 4000 rpm for 10 minutes, the adsorbent was removed to measure the amount of adsorbed phenol (29). The phenol concentrations were measured using PG Instruments T80 UV/VIS Spectrophotometer with calibration curve based on equation (1), at 505 nm wavelength (8,10).

Equation (1): $[\text{Phenol}] = 9.11 \times \text{UV absorption at } 505 \text{ nm} - 0.756$, ($r = 0.99$)

The surface morphology and chemical characterization of MR were carried out using scanning electron microscopy (Philips XL-30 SEM) (Figure 1). The surface area of MR area was calculated by the Brunauer-Emmett-Teller (BET) equation within the 0.05-0.30 relative pressure range (16). The amount of phenol adsorbed per unit mass of the adsorbent (q_e) was calculated by the following mass balance equation,

Table 1. The range of tested parameters

pH	Adsorbent dosage (g/L)	Phenol (mg/L)	Temperature ($^\circ\text{C}$)	Contact time (minutes)
3-12	0.1-1	100, 150, 200, 400, 600, 1000	30 ± 1	10, 30, 60, 80, 100, 120, 180

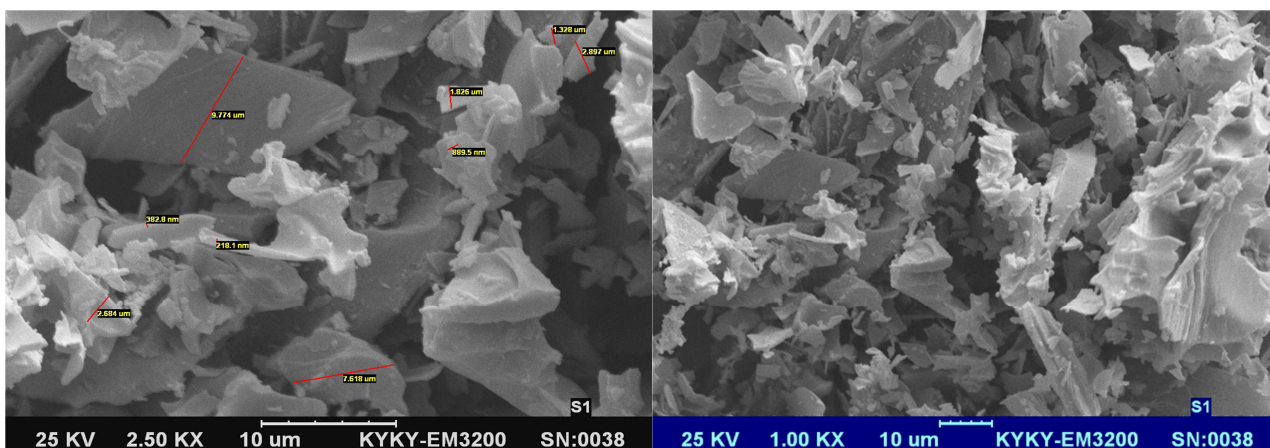


Figure 1. Scanning electron microscope micrograph of activated carbon of Meswak's root before adsorption

$$\text{Equation (2): } q_e = \frac{(C_i - C_e)V}{W}$$

And the percent adsorption of phenol was calculated as follows:

$$\text{Equation (3): } \text{Adsorption}(\%) = \frac{(C_i - C_e)}{C_i} \times 100$$

Where, c_i and c_e (mg/L) are the liquid phase concentrations of phenol at initial and equilibrium stages, respectively. V (L) is the volume of the solution, and W (g) is the mass of the dry adsorbent used. Langmuir and Freundlich isotherm models were used to estimate related parameters and identify the most suitable adsorption mechanism.

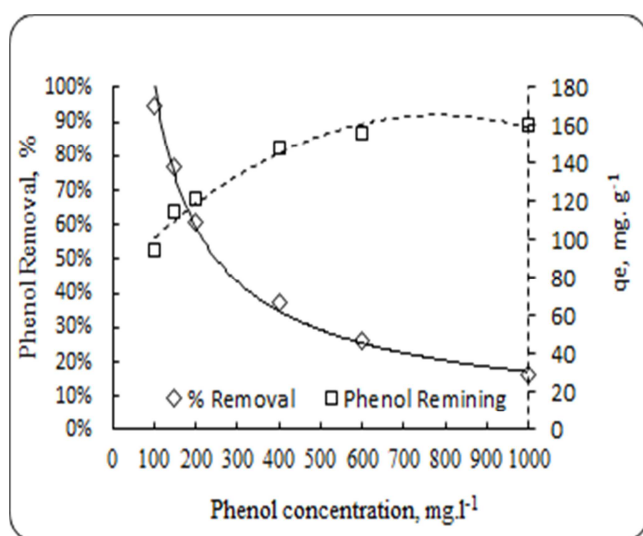


Figure 2. Effect change of phenol concentration (carbon preparation temperature = 800° C, adsorbent = 1 g/L, pH = 5, T = 120 minutes)

3. Results

In this study, adsorption of different concentrations of phenol in aqua solution using active carbon of MR treated with $KMnO_4$ was examined. What follows is a discussion of the results of experiments to find optimum value of the variables (Figures 1-8).

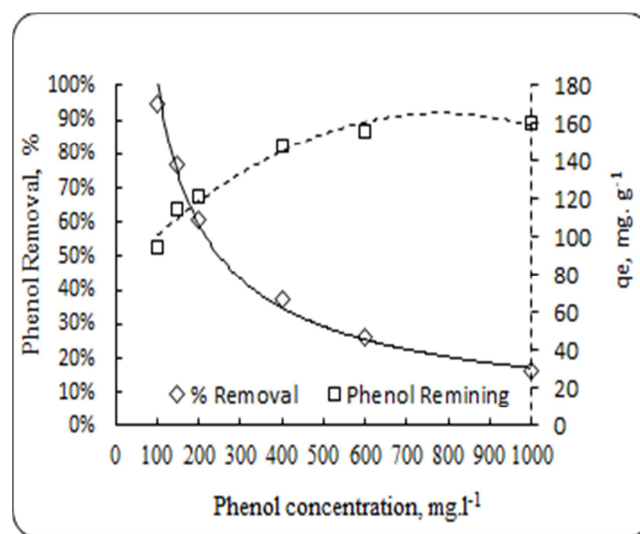


Figure 2. Effect change of phenol concentration (carbon preparation temperature = 800° C, adsorbent = 1 g/L, pH = 5, T = 120 minutes)

3.1. Characterization of activated carbon

An SEM micrograph of surface MR particles is shown in figure 1, which displays flask-type amorphous particles with smooth surfaces and pores. BET specific surface on the adsorbent were 1204 m²/g. Because the specific surface area of MR is low, the functional groups

likely have a more pronounced role than particle surface area in adsorbing phenol ions from liquid.

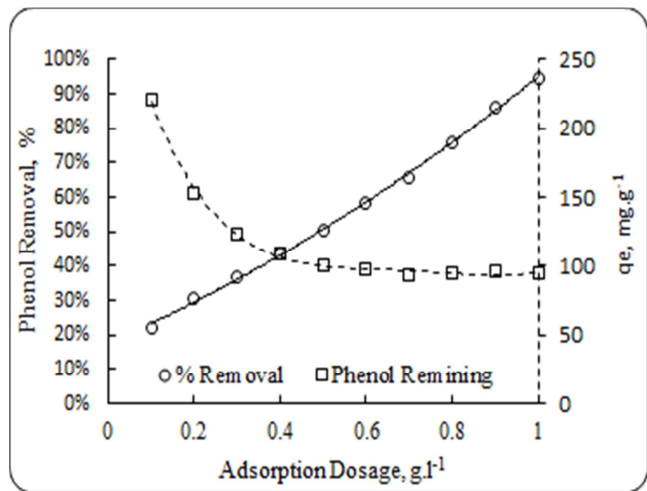


Figure 3. Effect of adsorbent dosage (carbon preparation temperature = 800° C, pH = 5, phenol concentration = 100 mg/L, T = 120 minutes)

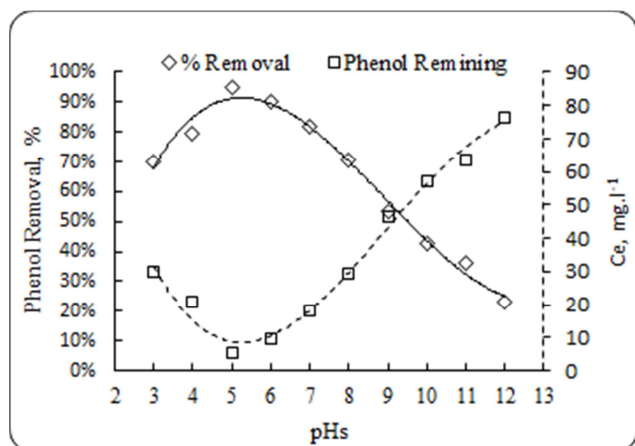


Figure 4. Effect of pHs (carbon preparation temperature = 800° C, adsorbent = 1 g/L, T = 120 minutes, phenol concentration = 100 mg/L)

3.2. Effect of the initial phenol concentration

The effect of the initial phenol concentration on the adsorption efficiency was shown in figure 2. This result revealed that by increasing the initial phenol concentration, the adsorption efficiency has a perceptible increase. The minimum and maximum efficiency of phenol removal were obtained about 16% and 94.76% when initial phenol concentration was fixed to 1000 and 100 mg/L, respectively.

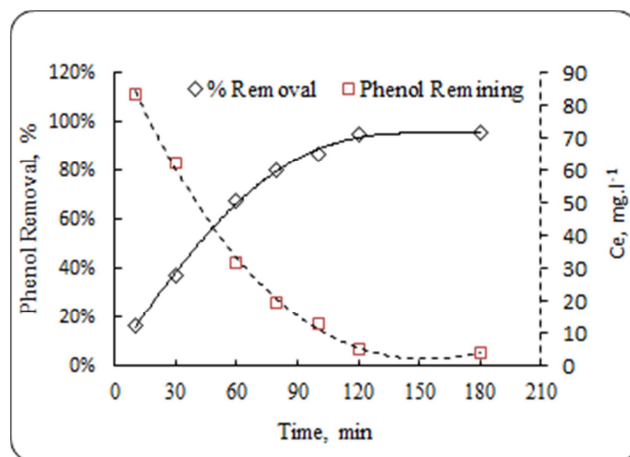


Figure 5. Effect of time (carbon preparation temperature = 800° C, adsorbent = 1 g/L, pH = 5, phenol concentration = 100 mg/L)

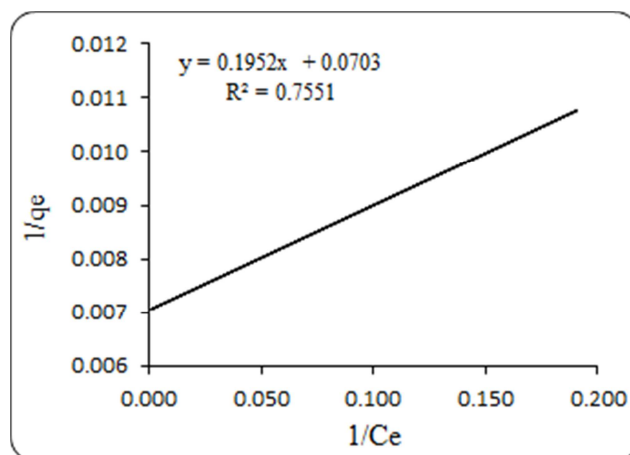


Figure 6. Langmuir isotherms fits the adsorption phenol (carbon preparation temperature = 800° C, adsorbent = 1 g/L, pH = 5, T = 120 minutes, phenol concentration = 100 mg/L)

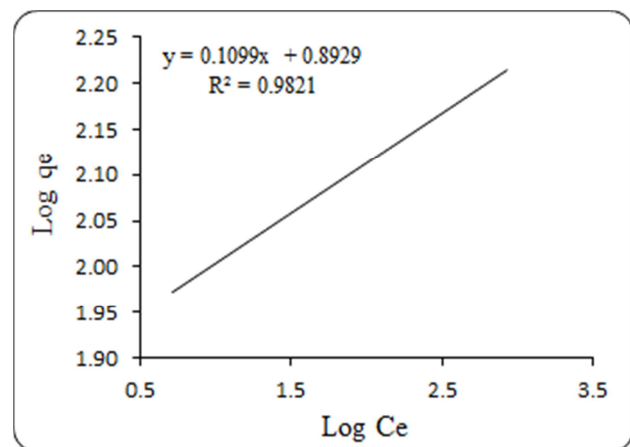


Figure 7. Freundlich isotherms fits the adsorption phenol (carbon preparation temperature = 800° C, adsorbent = 1 g/L, pH = 5, T = 120 min, phenol concentration = 100 mg/L)

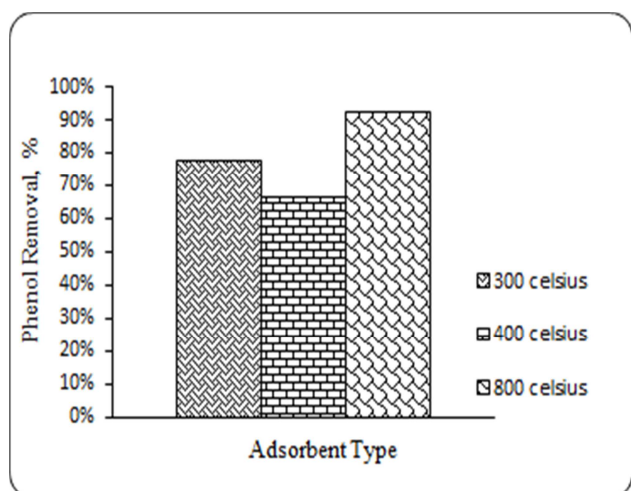


Figure 8. Effect of carbon preparation temperature (adsorbent 1 g/L, T = 120 minutes, pH = 5, phenol concentration = 100 mg/L)

3.3. Effect of MR adsorbent dosage

The adsorption of phenol was investigated by 0.1-1 g of adsorbent dosage. The effect of using adsorbent dosage on the adsorption rate was shown in figure 3. The maximum adsorption rate was achieved about 160 mg of phenol/1 g of MR when initial phenol concentration was fixed to 1000 mg/L. While at a 100 mg/L initial phenol concentration the adsorption rate was about 94.76 mg/1 g and 220.79 mg/0.1 g.

3.4. Effect of pH

The adsorption experiments in various pH of the phenol solution were done by keeping constant other laboratorial conditions including the phenol concentration, adsorbent dosage, carbon preparation temperature (CPT), and the contact time. The experiments in different pH showed that the removal percent of phenol changes with the change of pH (Figure 4). Optimum pH was 5.

3.5. Effect of contact time

The effect of contact time between the adsorbent and the adsorbate substance on adsorption efficiency was shown in figure 5. As shown in figure 5, the phenol adsorption increases with the increase of the contact time. It reaches equilibrium after 120 minutes with

94.76% efficiency of phenol removal. The most removal was obtained in 180 minutes about 96%. Therefore, optimum contact time was 120 minutes.

3.6. Isotherm models

Isotherm and adsorption capacity are of the main factors effective on adsorbents. To determine the isotherm models, Langmuir and Freundlich isotherms data obtained from the experiments with linear models adjusted the general case of linear equations in equations (1) and (2), respectively. The results of the model investigation are shown in figures 6 and 7, parameters of its calculated to base on the isotherm equations that are given in equations (1) and (2). Langmuir isotherm model forms onto layer adsorption while the Freundlich adsorption equation in a heterogeneous level of energy states. Clearly, adsorption follows the Freundlich model with correlation of 98.21%, and then the Freundlich model with correlation of 75.51%.

$$\text{Equation (1): } \frac{1}{q} = \frac{1}{q_m k_{ads}} \left(\frac{1}{c} \right) + \frac{1}{q_m}$$

$$\text{Equation (2): } \text{Log} q_e = \text{Log} k + \frac{1}{n} \text{Log} c_c$$

3.7. Adsorption isotherm

Surveying isotherm of adsorbent indicates how a contaminant is absorbed to the surface of adsorbent when the contaminant and adsorbent phases are at the balanced condition. Thereby, after determining optimum parameters, adsorbent isotherm was compared with Langmuir and Freundlich isotherm models (Table 2). A high correlation ($R^2 \approx 1$) indicates a high correlation of data with the isotherm model (22).

Maximum adsorption capacity with Langmuir and Freundlich isotherms and primary Phenol concentration of 100 mg/L were obtained 142.15 and 78.15 mg/g adsorbent, respectively. As the correlation curves of the two models show, phenol adsorption by active carbon of MR follows Freundlich isotherm.

Table 2. Parameters of Langmuir and Freundlich isotherm models

Freundlich isotherm			Langmuir isotherm					
K (mg/g) (L/mg)	n	R ²	Q (mg g ⁻¹)	B (L mg ⁻¹)	A	R _L	R ²	CPT
78.15	9.1	0.9821	142.15	14.22	0.36	0.00007	0.9001	800° C

CPT: Carbon preparation temperature

Under Freundlich model, “n” varies in the interval 1-10. The isotherm function is sound from mathematical viewpoint and value of 1/n is proportionate to adsorption intensity. Should value of “n” be in interval 0.1-1, there would be good consistency with the isotherm and surface adsorption (6). The value of R_L was in interval 0-1, which indicates proper adsorption of phenol on active carbon of MR. Value of 1/n and “n” were obtained equal with 0.109 and 9.1, which indicates acceptable consistency between active carbon of MR adsorbent and Langmuir and Freundlich isotherms (6). Active carbon of MR showed good Freundlich isotherms (R² = 0.98) correlation rather than Langmuir (R² = 0.75).

3.8. Effect MR carbon made at different temperatures on process performance

Figure 8 illustrates the effect of different CPTs on phenol adsorption performance. As pictured, preparing active carbon in furnace at 300° C, 400° C, and 800° C resulted in 92%, 78%, and 67% phenol removal.

4. Discussion

4.1. Effect of the phenol concentration and adsorbent dosage

Adsorbent dosage is one of the key parameters effective on adsorption capacity and balance point of contamination adsorption (9). It is a key driving force to overcome transfer strength of phenol from aqua to solid states (14). As illustrated in figure 3, steep linear increase of adsorbent dosage increases the performance of phenol adsorption. Phenol removal performance with an adsorbent dosage of 5 g/L and 10 g/L is about 71% and 77%, respectively. Kilic et al. (9) in the own

study reported that increase of adsorbent dosage resulted in an increase of adsorption performance up to a specific ceiling. They believed that due to increasing in a number of ion transfer sites and adsorption surface, an increase of adsorbent dosage resulted in an increase of adsorption capacity; however, in practice, aggregation of adsorbent particles reduced adsorption surface and adsorption capacity. Therefore, adsorption performance increases gradually with increase of adsorption dosage, and adsorption capacity decreases. Suresh et al. (5) in the own study reported that increase of adsorbent dosage resulted in decrease of adsorption capacity. They explained the findings by noting that decrease of adsorption capacity was due to available surface in its unsaturated form. Consistent with results of similar studies, our findings showed decrease of adsorption performance with increase of primary concentration, and in general, increase of contaminant concentration increased adsorption performance (7,9,14,29).

4.2. Effect of the pH

Adsorption pH is one of the key factors in the performance of surface adsorption of contaminations (16,18). Figure 5 illustrates the effect of different pHs on phenol removal by active carbon of MR. As pictured, increase of pH from 4 to 5 results in 35% increase in adsorption and further increase of pH is concomitant with gradual decrease of adsorption and 52% decrease of adsorption at pH 12. The highest phenol removal performance (95%) and lowest phenol removal performance (46%) are achieved at pH 5 and 12, respectively.

Chakraborty et al. (7) argued that the reason for the decrease of adsorption performance was due to the formation of impulsion force in an environment with extremely low and high pH and ionization of the adsorption and the contamination. They also stated that intensification of bounds between OH^- on adsorption surface with $\text{pH} > 5$ created negative charge; and adsorption of H^+ groups on adsorption surface with $\text{pH} < 5$ created positive charge; which in the both cases resulted in a decrease of phenol removal performance. In the study of Anbia et al. (2009), the highlighted formation of electrostatic forces between adsorbent and adsorption caused by pH effect and its effect on the performance of carbon adsorbents (30). Vinod and Varghese (2004) surveyed kinetic and balance specification of phenol on novel adsorbents and reported that with $\text{pH} > \text{pH}_{\text{pzc}}$ (point of zero charge), surface electrical load overcomes negative charges and given anionic nature of phenol, decrease of electrostatic adsorbent between phenol and adsorbent leads to decrease of adsorption performance. They also argued that with $\text{pH} < \text{pH}_{\text{pzc}}$ and through electrostatic force between adsorption and phenol, carboxylic factors increase adsorption performance (29). Kermani et al. (15) reported that the reason from decrease of performance in the acidic environment was neutralization of phenol ionization while the negative charge of phenol is responsible for the decrease of adsorption. They further reported, consistent with other studies, that optimum pH was 5. Kilic et al. (9) reported that by neutralizing sites with negative charges at attraction site, H^+ ions in highly acidic environment increased adsorption probability of phenol. They stated that pH ranges 5-9 was the optimum range for adsorption performance. Rodrigues et al. (2011) performed research and reported that with highly acidic pH, H^+ ions were attracted to carboxyl groups on the adsorbent surface and reduced number of adsorption sites (27). Hameed et al. (2008)

reported in the own study that pKa of phenol is about 9.89 and that ionization of phenol molecule competes with hydroxide ions to occupy adsorption surface in the environment with high pH, adsorption capacity decreases (31). Consistent with the studies above mentioned, our findings showed that the highest phenol removal performance was achieved with pH between 4 and 7, optimum pH was set at 5.

4.3. Effect of contact time

Figure 5 pictures performance of removal of phenol (mg/g adsorbent) with different contact time. Clearly, at beginning, adsorption performance and capacity of adsorption show higher growth rate, which decreases over time and reaches a balance point at 120th minute. The difference between phenol removal rates at 120 minutes and 180 minutes is about 0.01 mg/g adsorbent. The figure 5 indicates that highest concentration of phenol remaining over 180 minutes was 3.69 mg/g. Several studies have focused on contact time (14,23,31-35). Contact time between 10 and 180 minutes and its effect of adsorbent performance and adsorption capacity are pictured in figure 3. Kermani et al. (15) argued that carbon adsorption rate at the beginning of the process was very high and decreased gradually up to 120th minute where balance point was achieved. They stated that the reason for their finding was the formation of a layer of phenol on the adsorbent. In a study of Lio et al. (2011) reported that adsorption rate hit the top 90 minutes after initiation of the process and followed a descending trend afterward until balance point at 120th minute (25). Other studies have reported consistent findings (2,9,14). Given the consistency of our findings with other studies, optimum contact time and balance point were set at 120 minutes and 180 minutes.

5. Conclusion

The results of the investigations show that the

optimal conditions for the degradation of 100 mg/L of phenol with 94.76% efficiency were pH = 5, CPT 800° C, MR adsorbent dosage 1 g with a contact time of 120 minutes at lab temperature. Furthermore, the results showed that the amount of phenol, adsorbed by the adsorbent type is under the influence of various parameters such as pH, initial phenol concentration, contact time, and the amount of the adsorbent. So that phenol removal efficiency has a direct relationship with the increase in the adsorbent dose, contact time and temperature, an inverse relationship with increased pH, and concentration of the phenol. Adsorption equilibrium data, obtained in this study for adsorbent followed Freundlich isotherm ($R^2 = 0.9821$). So, the activated carbon produced from the MR treated with $KMnO_4$ with high efficiency and output, minimal use of chemicals, and with little time has the ability to adsorb and remove the maximum phenol.

Conflict of Interests

The Authors have no conflict of interest.

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