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A feasible study on the application of raw ostrich feather, feather treated with H_2O_2 and feather ash for removal of phenol from aqueous solution

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ABSTRACT

Phenol, one organic pollutant, is extremely toxic for humans and the environment. The removal of phenol and its compounds from water and wastewater is serious problem. In this study, ostrich feather was used as the sorbent for the removal of phenol from aqueous solutions. For this purpose, raw ostrich feathers (ROF), feather treated with H_2O_2 (TOF) and its ashes (OFA) were used. In this study, ostrich feather was used in doses 0.2, 0. 3, 0 .5, 0.7, 1 and 1.5 $\frac{g}{100ml}$. Also, effect of different variables such as pH, contact time, amount of sorbent and temperature has been determined. Then, accuracy of data was examined by Freundlich, Langmuir and BET equations. Optimum phenol adsorption was observed at pH 2 and pH 3 for ROF/ TOF and OFA, respectively. Results showed that 0.7 g of ROF and TOF and 2 g of OFA removed 83, 73 and 90.4% at 30°C after 24 h, respectively. Results also indicated that ostrich feather, as a solid waste of the poultry processing plant, can be used as an effective biological sorbent for phenol removal from aqueous solutions.

Keywords: Phenol; Feather; Isotherm; Adsorption

1. Introduction

Industrial effluents often contain significant amounts of organic pollutants such as phenol and its derivatives that provoke disastrous problems for animal and human health. This aromatic compound is the main component in coal tar process [1]. Phenol and phenolic compounds are mostly generated in the petroleum and petrochemical products, the manufacture of dyes, plastic, pesticide and aspirin [2]. Phenol is highly soluble in water and its presence in water sources, which is identified from various aspects such as taste, smell, color; is harmful to organisms and causes human deaths even at low concentrations. Phenol is a disastrous stimulant and corrosive compound for skin, eye and respiratory tract thereupon direct contact. Also, chlorophenol is produced during chlorination of water. Therefore, phenol and phenolic compounds were designated as priority pollutants by the EPA. According to water quality standards, concentration of phenol compounds in drinking water should not surpass the order of μg/L [3–5]. Phenolic combination cannot be separated from water during conventional treatment processes. Generally, there are many methods for the treatment and removal of phenol, they are: adsorption and ion exchange, solvent extraction, oxidation and biological processes such as application of microorganisms [6]. During recent decades,

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many studies were undertaken about phenol and other organic pollutants removal by using cheap and accessible sorbent materials. These cheap sorbent can be noted as industrial and agricultural wastes such as sugarcane ash [7], over granulated waste materials [8], eggshell [9] and even birds feathers [10]. In fact, feather is a natural sorbent with a protein content of around 84% [11]. Thus in the present research, ostrich feather has been used as an available material and a low-cost biological sorbent from poultry processing plants for the removal of organic pollutants and heavy metals [12]. In Iran, there exist about 3,000 units of ostrich farming that annually generate huge amounts of feather waste. Therefore, we aimed at investigating the ability of ostrich feather for removing phenol from aqueous solutions and determining the potential of ostrich feather in the phenol removal from wastewater.

2. Material and methods

2.1. Preparation of the biosorbent

Ostrich feathers used in this research were obtained from a poultry processing plant. Feathers were used in three different ways including: raw feather, treated feather with H_2O_2 and feather ash. First, the aw feathers were washed with a detergent then washed several times with distilled water and dried in the sunlight for 1 day. Then dried feathers were cut carefully, sieved with 0.5 and 0.3 cm sieves and finally sorbents of 0.3 cm size were achieved. In the second step, for removing the attached organic materials, washed and dried soft barbs of feathers were treated with 30% (w/v) hydrogen peroxide for about 18 h, then this sorbent was washed with distilled water and then feathers were kept in oven at 100°C for 12 h to be dried. Finally, the prepared sorbent was kept in desiccator until the time of experiment. In the third step, the ostrich feather was burned at 550°C for 15 min. Also, this sorbent was kept in desiccator until the time of the experiment.

2.2. Study steps

Sorption experiments were carried out in batch technique. Phenol adsorption in aqueous solution in raw feather, treated feather and feather ash was examined using various parameters such as: pH (2, 3, 7 and 9), temperature (20, 30 and 40°C), contact time (0.5, 2, 4, 8, 16, 24, 25 and 30 h), dosage of sorbent (0.2, 0.3, 0.5, 0.7, 1 and 1.5 g) and concentration of phenol (1, 5, 15, 25 and 50 mg/L). Finally, the effect of this biosorbent in the various chemical oxygen demand (COD) test was studied.

A stock phenol solution of 1,000 mg/L was obtained by dissolving 1 g phenol (Merck Germany) in 1 L of distilled water. Phenol solutions in the concentration range of 1–50 mg/L were prepared from dissolving the stock solution in distilled water.

All experiments were carried out using the constant phenol concentration (15 mg/L). Phenol solution with the constant concentration of phenol was transferred into 250 mL bottles and known dosage of sorbents was added to each bottle. A shaker was used for mixing the sorbent and phenol solution. Then the samples were placed in the incubator for temperature control. Finally, after achieving a balanced mixture, the bottles were taken from incubator for future experiment. Then the feathers were separated from the solution by Whatman filter paper No. 42. The concentration of residual phenol in the solution was measured using a spectrophotometer (spectrophotometer DR-5000, HACH). This process was based on the developed colour resulting from the reaction of phenol with 4-aminoantipyrine at 500 nm. All the experiments were conducted in triplicate, and the average results are reported in this paper. Finally, the phenol concentration was calculated using:

$$\text{Phenol } \frac{\text{mg}}{\text{L}} = C \times D \times \frac{1000}{E} \times B \quad (1)$$

Where C: mg standard phenol solution, D: sample absorbed sorbent, E: absorbed standard phenol solution, B: applied milliliters for main sample

3. Results and discussion

3.1. Effect of pH

Fig. 1 shows the pH effect on the adsorption of phenol by ROF, TOF and OFA. According to Fig. 1, the percentage removal of phenol decreased with increase in pH from 2 to 9 for ROF and TOF. Also for OFA, phenol uptake increased by increasing pH from

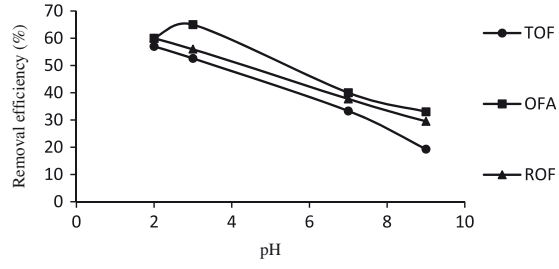

Fig. 1. Effect of pH on the removal of phenol by ROF, TOF and OFA (initial phenol concentration: 15 mg/L, contact time: 8 h, sorbent dosage: 0.5 g and temperature: 30°C).

2 to 3, while efficiency decreased from pH 3 to 9. When pH was increased between of 7 and 9 a significant decrease in phenol removal efficiency was observed. As shown in Fig 1, at low pH range (2 and 3), adsorption efficiency was high. This is due to pH effect on the surface charge of the sorbent and also can be ascribed the impact of phenol ionization on the pH value. In the lower pH values, the surface of the sorbent would be encompassed by positive charge and a strong attractive force would occur between positive charges in the sorbent and negative ions in the phenol [10,13–15]. The ionic section of phenol (φ_{ions}) can be calculated according to the following equation [13,16]:

$$\varphi_{ions} = \frac{1}{[1 + 10^{(pK_a - pH)}]} \quad (2)$$

According to the above equation, while the pH is increased, φ_{ions} amount increases, whereas, phenol is a weak acid with $pK_a = 10$, a minor amount of phenol will be absorbed at higher pH [13,14,16]. Also during experiment, it was observed that with pH increase towards the neutral and alkaline values turbidity in solutions increased, which may be due to the effect of pH on the feather compounds and the dissolution of the some feather compounds such as fat in water.

3.2. Effect of temperature

The results were given in Fig. 2 to show the effect of temperature on the rate of phenol removal during various times (2–8 h). As seen from figure, with an increase in temperature from 20°C to 30°C, the removal efficiency increased and with higher increase of temperature from 30°C to 40°C, the percentage removal decreased. This increase in efficiency can be due to the stretching of ostrich feather, the increase of phenol dissociation and thus increase of more available active sites in the sorbent [10,17]. As seen from results, with an increase in temperature to 40°C, phenol removal reduced in these processes. This decrease in percentage removal with temperature indicated that the adsorption process was exothermic. With higher increase in temperature, the phenol motion and movement would increase and may be a weakening force between the available sites of the sorbent and phenol [17,18].

3.3. Effect of sorbent dosage

Fig. 3 shows the effect of sorbents dose on the removal of phenol at 30°C. It is observed from the figure that the adsorption of phenol increased with increase in the adsorbent amount of ROF and TOF from 0.2 to 0.7 g. While, it is observed that after an dosage increase from 0.7 to 1.5 g, there was reduction in the phenol removal efficiency. Thus, 0.7 g was chosen as optimum amount for this sorbents. Results were different for the feather ash. As seen from Fig. 3, phenol removal increased with increase in the sorbent dosage from 0.2 to 2 g and by increasing ash dosage from 2 to 3 g, removal efficiency decreased. Thus, optimum dosage for ROF, TOF and OFA was obtained as 0.7 and 2 g, respectively. This increase in phenol removal efficiency by sorbent dosage is due to increase of the active sites in sorbent surface for phenol adsorption and thus more phenol is attached to their surface [10,18,19]. Also, decrease in removal rate with increasing dosage may be due to the shortage of active sites at higher sorbent amounts [20].

3.4. Effect of contact time

Phenol adsorption in different contact time was studied for a sorbent dosage of 0.2 – 1 g. Results are presented in Figs. 4–6. It is definite from the figures that the sorption efficiency increased with increasing

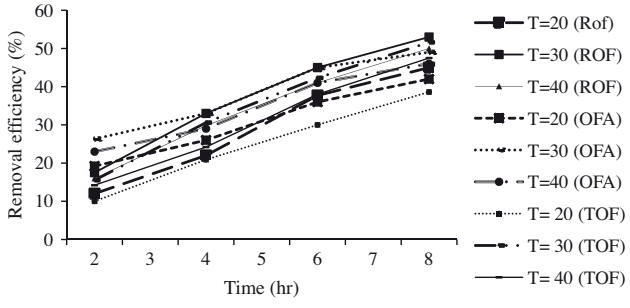

Fig. 2. Effect of temperature on the phenol uptake at different times (initial phenol concentration: 15 mg/L, contact time: 2–8 h, sorbent dosage: 0.5 g/100 mL and pH: 2 (for ROF and TOF) and pH: 3 (for OFA)).

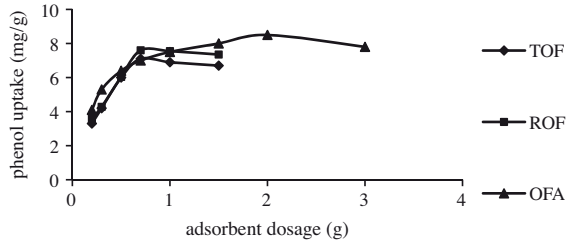

Fig. 3. Effect of amount of ROF, TOF and OFA on the removal of phenol (phenol concentration: 15 mg/L, contact time: 8 h, temperature: 30°C and pH: 2 and 3 (for feather ostrich, feather treated by H_2O_2 and its ash, respectively)).

contact time. According to results, the equilibrium time for the adsorption of phenol in initial concentration of 15 mg/L was obtained in 24 h on all the three sorbents. As seen from figures, the rate of phenol removal occurs in the first 16 h on contact and afterward, only a gradual increase of adsorption is seen until about 24 h and also a constant trend in the adsorption rate was observed after 24 h. The increase in the rate of removal in the first 16 h may be due to the increase in number of available vacant sites and also the concentration gradient between solute and sorbent surfaces was high. Gradually, as time passes, these sites on the sorbent are filled up by phenol ions and the concentration gradient would decrease, thus in the equilibrium time, the rate of sorption is equal to the rate of desorption [10,16,21].

3.5. Effect of initial phenol concentration

In this study, the adsorption capacity of ostrich feather was investigated from 1 to 50 mg/L with optimum sorbent dosage at temperature 30°C. The results are presented in Figs. 7–9. The results indicate that percentage removal of phenol decreased with increase in initial phenol concentration from 10 to 50 mg/L on all the three sorbents. The higher removal rate of phenol in lesser concentrations can be ascribed to the exits the more active sites on the sorbent surface for low value of phenol, also this objective may be dependent on the increase in the mass transfer velocity in lower phenol concentrations [10,13].

3.6. Adsorption isotherms (Freundlich, Langmuir and BET)

There are several models to describe experimental data and the most important models are adsorption isotherms. Analysis of adsorption isotherms in order to reach an equation, which shows the accurate results and design adsorption systems is very important

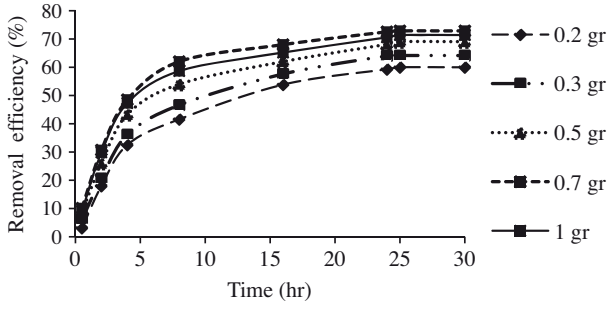

Fig. 4. Effect of contact time on the phenol uptake ROF (phenol concentration: 15 mg/L, temperature: 30°C, ROF dosage: 0.2–1 g and pH: 2).

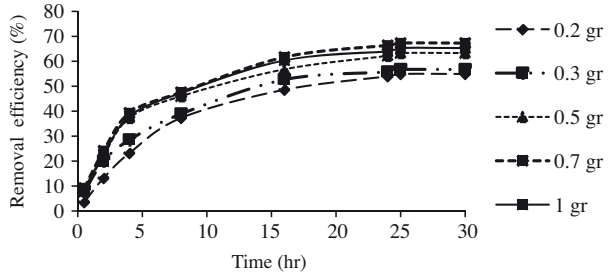

Fig. 5. Effect of contact time on the phenol uptake TOF (phenol concentration: 15 mg/L, temperature: 30°C, TOF dosage: 0.2–1 g and pH: 2).

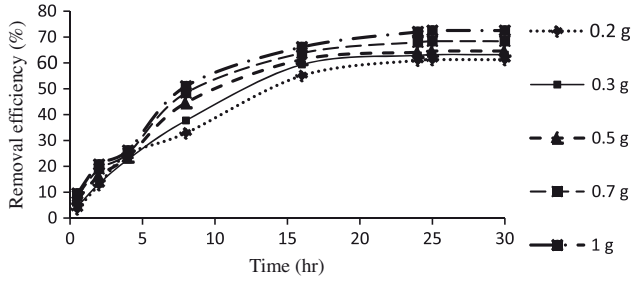

Fig. 6. Effect of contact time on the phenol uptake OFA (phenol concentration: 15 mg/L, temperature: 30°C, OFA dosage: 0.2–1 g and pH: 3).

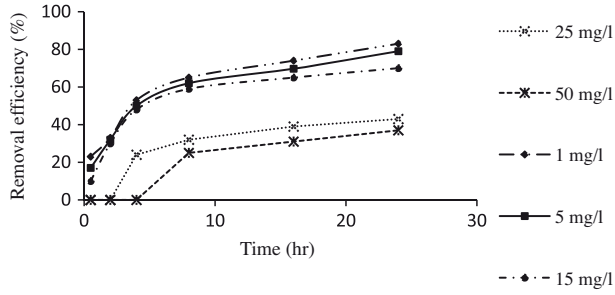

Fig. 7. Effect of initial phenol concentration on phenol uptake (raw feather dosage: 0.7 g, temperature: 30°C and pH: 2).

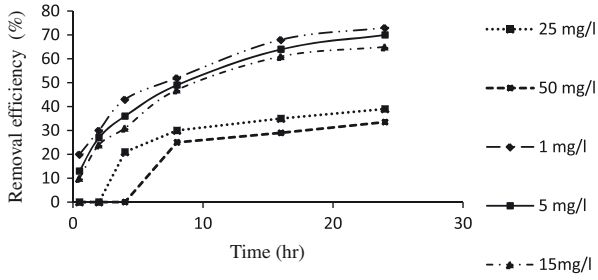

Fig. 8. Effect of initial phenol concentration on phenol uptake (feather treated with H_2O_2 dosage: 0.7 g, temperature: 30°C and pH: 2).

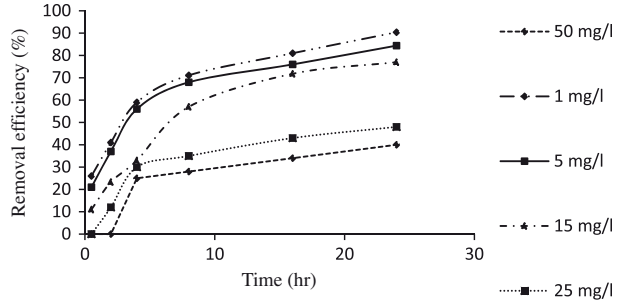

Fig. 9. Effect of initial phenol concentration on phenol uptake (feather ash dosage: 2 g, temperature: 30°C and pH: 3).

[13,22]. Adsorption isotherms can be described based on the explanation for change in adsorption of the adsorbate by the adsorbent in solution. Analyses of the isotherms are momentous to develop and display the result accurately for design objects [23].

For this purpose, data obtained from the adsorption phenol were tested by Freundlich, Langmuir and BET isotherms. These isotherms were obtained from the following methods:

The linear form of Freundlich isotherm is:

$$\log q_e = \log K + \frac{1}{n}\log C_e \quad (3)$$

Where: q_e is the constant adsorbed of equilibrium in soil phase (mg/g), C_e is the equilibrium concentration of the sorbent in liquid phase (mg/L), and K and $1/n$ are the Freundlich constants which K is the adsorption capacity (mg/g) and $1/n$ is the intensity of adsorption This constant (K and $1/n$) obtained from the intercept and slope, respectively, and determined from the intercept and slope, respectively of linear plot of $\log q_e$ vs. $\log C_e$ (13, 24, 25).

The linear form of Langmuir isotherm is:

$$\frac{1}{x/m} = \frac{1}{b} + \frac{1}{aQc} \quad (4)$$

Where: Q (mg/g) and b (L/mg) are the Langmuir constants. These constants evaluated by the intercept and slop of the linear plot of the experimental data of $1/x/m$ vs. $1/C$ (13, 24, 25).

The BET isotherm is:

$$\frac{c}{(C_s - C)q_e} = \frac{1}{BQ^o} + \left(\frac{B-1}{BQ^o}\right)\left(\frac{C}{C_s}\right) \quad (5)$$

Where: C_s is the saturation concentration of the soluble matter (mM), C is the soluble matter concentration

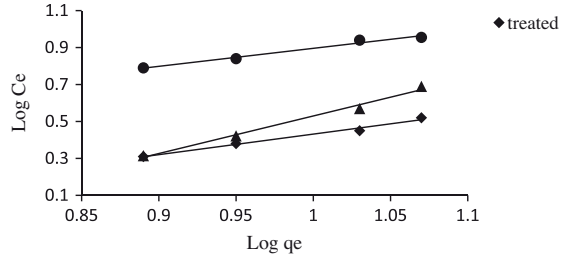

Fig. 10. The linearized Freundlich adsorption isotherm for phenol removal by ostrich feather, feather treated with H_2O_2 and their ash.

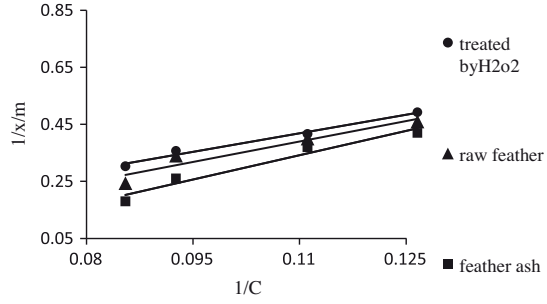

Fig. 11. The linearized Langmuir adsorption isotherm for phenol removal by ostrich feather, feather treated with H_2O_2 and their ash.

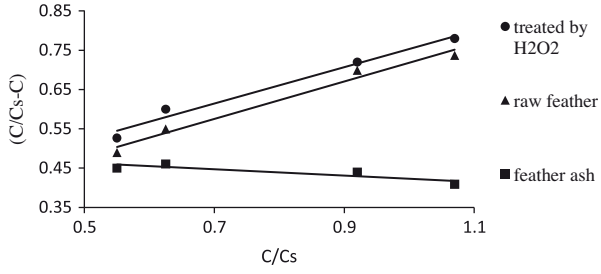

Fig. 12. The linearized BET adsorption isotherm for phenol removal by ostrich feather, feather treated with H_2O_2 and their ash.

in equilibrium (mM), $Q°$ is number mMols matter absorbed per unit mass of adsorbent (g) for structure on absorbent layer (mMol/g) and q_e is total mMol substance absorbed per unit mass of adsorbent (g) are in equilibrium (mMol/g) [26].

As seen from Figs. 10–12, phenol adsorption in all processes obeys Freundlich isotherm. However, according to the amount of coefficient regression (R^2) which is presented in Table 1, all of three equations are suitable for description of phenol adsorption for these sorbents. Moreover these

Table 1
Parameters of Freundlich, Langmuir and BET isotherm models

	Freundlich constants			Langmuir constants			BET constants		
	K (mg/g)	$1/n$ (mg/L)	R^2	a (mg/g)	b (L/mg)	R^2	$Q°$ (mMol/g)	X_m	R^2
Raw feather	0.22	0.75	0.980	0.64	3.57	0.919	1.87	1.16	0.979
Feather treated with H_2O_2	0.24	1.4	0.985	2.16	3.7	0.983	1.26	1.62	0.979
Feather ash	0.04	4.5	0.990	1.39	20	0.956	–	–	0.783

results indicated that feather ash did not comply with BET isotherms. For these sorbents the constants regression was higher than 0.9. But results related to Freundlich isotherm models represent a more reliable physical description for absorbing pollutants which could be due to the presence of adsorption bands in the sorbent. According to the results, Freundlich isotherm due to higher R^2 value (0.989) can best describe the phenol adsorption data than Langmuir isotherm and BET isotherm. The results also show that ostrich feather ash does not comply with the BET isotherm.

3.7. Effect of feather on COD in solution

Effect of the feather on solution organic load was studied and shows that this sorbent has less effects on increasing the organic load of solution. The experiments show that 0.7 g/L of biosorbent causes an increase of 20 mg/L COD in deionized water at 4 h for ROF. This may indicate that feather and its compounds are insoluble relatively and have low dissolution in solution [11,27].

4. Conclusion

Ostrich feathers can be used for the removal of phenol in aqueous solution. Adsorption capacity in this sorbents was dependent on the pH and there was an increase in phenol removal efficiency with a decrease in pH. According to the results, it is observed that by increasing the amount of sorbent, the efficiency of removal of phenol would be increased. The equilibrium time for phenol removal was found to be 24 h. According to the results, it was observed that the OFA had the highest removal efficiency than ROF and TOF.

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