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Removal of nonylphenol from aqueous solutions using carbonized date pits modified with ZnO nanoparticles

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ABSTRACT

The adsorption process is a convenient and efficient method for the removal of phenolic compounds. This experimental research investigated the removal of nonylphenol using nanoparticles of zinc oxide-modified date pits. Variables were initial nonylphenol concentration, time, pH, and adsorbent dosage. To adsorb nonylphenol from aqueous solutions, date pits and date pits modified with nanoparticles of zinc oxide were used. Adsorption isotherms and adsorption kinetics were also examined. Both adsorbents were characterized using scanning electron microscopy, Brunner-Emmett-Taller, and X-ray diffraction. Nonylphenol concentrations of samples were determined using ultra-high performance liquid chromatography after the adsorbents were added. Maximum removal efficiency of nonylphenol by modified date pits under optimal conditions including contact time of 60 min, pH = 6, concentration of 1.35 mg/L nonylphenol, and an adsorbent amount of 10.1 g/L were 95% for synthetic and 74% for real samples, respectively. The nonylphenol removal efficiency under optimal conditions of wastewater from the campus of Kerman University of Medical Sciences was reported as 74%. The adsorption reaction of nonylphenol by date pits followed the Freundlich isotherm and pseudo-second-order models. Modified date pits are a good adsorbent and can be recommended as an efficient adsorbent for the removal of nonylphenol.

Keywords: Nonylphenol; Adsorption; Date pit; Zinc oxide

1. Introduction

Environmental pollution caused by endocrine disrupting compounds (EDCs) in water sources and industrial wastewater output has become a public concern [1]. EDCs, as one of the most hazardous pollutant groups in wastewater and water resources around the world, are produced naturally or as a result of human activities and can cause disorderliness in the activities of endocrine systems of wildlife and humans. Among different types of EDCs, nonylphenol (NP) has been categorized as an important disruptor of endocrine glands. NP is prone to disrupting the hormone system, and it is an imitator of the hormone estrogen in many organisms. NP is produced at a high level and is used as a chemical interface for the production of nonylphenolethoxylate (NPEs) [2,3]. The structure of this compound is shown in Table 1.

NPEs are important non-ionic surfactants used largely in industry for the production of such items as detergents, liquid soaps, cosmetics, dyes, and as a spraying agent in pesticides and herbicides. NP is known as a resistant material against aqueous media, bio-accumulative material, and a very poisonous substance for aquatic organisms. Nonylphenol is used as a monomer for the production of plastic substances, especially bottles of mineral water and disposable dishes [4,5]. Due to the extensive application of this compound in many industrial and commercial products,

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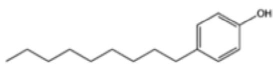
Table 1
Basic physical and chemical properties of nonylphenol

Formula	$C_{15}H_{24}O$
Molecular structure of NP	
Molecular weight	220.35 g/mol
Appearance form	Liquid
Melting point/freezing point	Melting point/range: 158–159°C - lit.
Initial boiling point and boiling range	302°C at ca.1.01 hPa
Relative density	0.93 at 25°C
Water solubility	0.0049 g/L - slightly soluble

it has been reported in different environmental matrices including weather, water, sludge, soil, dust, foods, drinks, and even in human samples [6]. The adverse effects of NP on human health and reproductive biology include breast and prostate cancers, reduction of sperm count, reduction of fertility in men, early puberty in women, behavioral problems, a prevalence of obesity, and defects in the immune system [7,8]. It is not possible to remove NP completely due to its complex molecular aromatic structure and low biodegradability [9]. Among filtration methods, the efficiency of biological methods is not satisfactory because of the high toxicity of NP for aerobic and anaerobic bacteria [12], and ultra filtration and reverse osmosis are not cost effective [10–13]. Many different methods have been used to remove this material, including advanced oxidation methods such as the Fenton and electro-Fenton methods [14], ozonation with ultraviolet light [15], the use of catalysts [16], and adsorption methods such as activated carbon, chitosan, and nanoparticles [17,18]. The adsorption process is a priority because of its lower initial cost, simplicity of operation, lack of harmful secondary production, low sensitivity to stream fluctuations, the ineffectiveness of toxic chemicals in the process, and the removal of most organic materials. Among the different adsorbents, activated carbon has a significant importance due to its high adsorption capacity, but because of its high costs, natural adsorbents such as agricultural waste and industrial waste have been noticed [19].

The use of ash as a low-cost adsorbent for the removal of phenolic compounds is recommended [20,21]. Its low cost makes it a good alternative for activated carbon. One of these bioadsorbents is the date pit. Studies have shown that carbon produced from date pits has a remarkable ability to adsorb contaminants. The use of nanoparticles to improve the performance of adsorbents has been considered, including the use of iron and carbide nanoparticles on carbon to remove arsenic [22–29].

In China, Ran et al. (2015) studied the biological adsorption of nonylphenol by algae and planktons. In Hong Kong, Chu et al. (2016) studied the degradation of nonylphenol available in water using sonophotolysis technology. In Spain, Rosa et al. (2010) studied and compared the effects of advanced processes of oxidation and chlorination on the removal of nonylphenol from drinkable water. In China, Xiao et al. (2013) studied the removal of phenol from water by through ozone. In Turkey, Fadime et al. (2016) studied the process of biological degradation of nonylphenolethoxylate on anaerobic digesters in a wastewater treatment plant. Malakootian et al. conducted extensive research in Iran using different methods to the removal of phenol, phenol derivatives, heavy metals, and antibiotics from water and wastewater [30–35].

According to scientific sources, no study has been done in the field of NP adsorption using modified-carbonized date pits with ZnO nanoparticles (MCDP).

2. Experiments

2.1. Materials

NP (100% purity) and ZnO nanoparticles (40 nm) were purchased from Sigma-Aldrich. The Solution pH was calibrated by HCl and NaOH 0.1 M. The date pits used in this study were purchased from the Pastry Shop Center. Table 1 shows information on basic physical and chemical properties of NP.

2.2. Analytical methods

The pH of solutions was measured by pH meter (model: HANNA). A magnetic stirrer (model: Fan Azmagostar) was used for stirring. A scale model Shimadzu-Libror was used to weigh chemicals.

2.3. Preparation of adsorbent

Date pits were washed and rinsed several times in double-distilled water to remove pollutants. Then, they were placed in an oven at 100ºC for 24 h to remove moisture. The dried kernels were ground with a powder mill. To stabilize the nanoparticles on the adsorbent, the immersion method was used; 500 cc of double-distilled water was poured into a flask and 1 g of nanoparticles was added. The solution was stirred at 300 rpm for 30 min. Then, 100 g of prepared powder was added to the solution, and it was mixed again for 1 h. After that, the prepared powder was placed in an oven at 100ºC for 24 h to remove its moisture. The dried powder was placed in an electric furnace at 700ºC for 2 h to stabilize the nanoparticles on the adsorbent and to prepare the adsorbent [32,36,37].

2.4. Characterization methods

To measure the porosity of the surface area adsorbents, the Brunner-Emmett-Taller (BET) method using a Micrometrics Model 021LN2 transfer device was employed. The surface areas of adsorbents were determined by nitrogen adsorption at a temperature of 77 K. To determine the presence and percentage of zinc oxide nano-particles on the carbon adsorbent, X-Ray Diffraction (XRD) with a Philips X-Pert device made in the Netherlands was employed [32]. Scanning Electron Microscopy (SEM) test using an EM3200 Model device made by KYKY Company was done in order to examine the microscopic structure on activated carbon and fixed nanoparticles on activated carbon.

2.5. Experimental practices

First, the nonylphenol stock solution (1000 mg/L) was prepared, and then other solutions were prepared with the intended concentrations. Batch experiments were conducted in flasks with a volume of 100 mL, a mixing speed of 250 rpm, and a temperature of 25ºC. To prepare the stock solution, NP was first solved in 2 cc methanol because of its very low solubility in water and then brought to volume with distilled water. The stock solution was kept in the dark at 4ºC [36,38,39].

After adding the required amount of adsorbent to each sample, the adsorbent and NP were thoroughly mixed using a magnetic stirrer at a speed of 250 rpm. Adsorbent was separated from the samples using centrifuges at a speed of 1400 rpm for 15 min. Then the samples were passed through filter paper with a pore size of 0.45 µm. Sample concentrations of NP were determined using a Ultra-High Performance Liquid Chromatography (UHPLC) device (AZURA model, KNAUER, GERMANY) under the following conditions:

Column: Ascentis Express C18, 10 cm*2.1 mm I.D., 2.7; mobile phase: water: acetonitrile (50:50); flow rate: 0.4 mL/min; pressure: 3268 psi (225 bar); column temperature: 35ºC; detector: UV (280 nm); injection: 1 µL.

The adsorption capacity and removal percentage of NP onto adsorbent were calculated using Eqs. (1) and (2)**:**

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

$$\% R = \left(\frac{C_o - C_e}{C_o}\right) \times 100 \quad (2)$$

where q_e is the adsorption capacity of MCDP for the NP solution (mg/g), C_0 is the initial concentration of the NP solution (mg/L), C_e is the equilibrium concentration in the NP solution (mg/L), m is the mass of MCDP (g), V (L) is the volume of the NP solution, and R (%) represents the removal percentage of NP on MCDP.

2.6. Reusability of adsorbent

The method used in this study is reactivation, which involves heating the spent carbon in a high temperature (815ºC) furnace. The contaminants are vaporized, restoring the carbon original pore structure, allowing for its reuse [40].

2.7. Adsorption isotherms and adsorption kinetics

Two isotherm equations were used to determine the Langmuir and Freundlich models. Both of models are shown in Eqs. (3) and (4), respectively.

$$\frac{C_e}{q_e} = \left(\frac{1}{Q^o b}\right) + \left(\frac{C_e}{Q^o}\right) \quad (3)$$

$$Log(q_e) = Log(K_f) + \frac{1}{n} Log(C_e) \quad (4)$$

where C_e and q_e, respectively, are equilibrium concentration and equilibrium adsorption capacity (mg/g), Q^o is maximum equilibrium adsorption capacity of NP on the surface of MCDP (mg/g), and b shows the correlation energy adsorption (L/mg). K_F and n are Freundlich constants; K_F is associated with adsorption capacity (mg/g) (L/mg) 1/n, and n shows the tendency to adsorb.

Pseudo-first-order and pseudo-second-order models were used to determine the adsorption kinetics. The linear forms of both models are shown in Eqs. (4) and (5), respectively.

$$Log(q - q_e) = Log(q_e) - K_1 \cdot \frac{t}{2.303} \quad (5)$$

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

where q_e is the NP adsorbed by the MCDP (mg/g), q_t is the NP adsorbed by the MCDP (mg/g) at time (min), K_1 (min^{-1}) and K_2 (mg/(g·min) are the constants of the equilibrium rate of first- and second-order kinetics, respectively [41,42].

2.8. Design of experiments

Screening tests were performed using the software Minitab17. Then, the removal of NP was optimized using the response surface method (RSM) with the Box-Behnken model. Data analysis was performed using Minitab17 and Excel 2013. To prevent systemic errors, experiments were performed in random order with three replicates [43].

3. Results and discussions

3.1. Characterization of adsorbent

Information obtained from the BET test showed that surface area, pore volume and pore size were 34.91 m²/g, 0.03 cm³/g and 1.57 nm respectively. Surface area is created by division of particles (size reduction) and the generation of porosity and is destroyed by sintering melting, etc. The results of BET analysis for surface area and porosity are shown in Table 2.

XRD test was performed and confirmed the modifying of the adsorbent well. As shown in Fig. 5, new peaks were appeared in the graph after modifying the adsorbent that proved the presence of zinc oxide nanoparticles on the

Table 2
Porosity and surface area of BET analysis using modified-carbonized date pits

Surface area	
BET surface area	34.91 m²/g
Langmuir surface area	41.76 m²/g
Pore volume	
Single point adsorption total pore volume of pores	
t-Plot micropore volume	0.03 cm³/g
Pore size	
Adsorption average pore diameter (4V/A by BET).	1.57 nm

surface is adsorbent. The results of XRD analysis of CDP, MCDP, and ZnO nanoparticles are shown in Figs. 1a and 1b respectively [32].

SEM test was performed and confirmed the modifying of the adsorbent well. SEM test showed absence of impurities in the zinc oxide nanoparticles used in this study. SEM image of pure activated carbon shows that this absorbent is porous in nature. SEM image of zinc oxide nanoparticles on activated carbon shows that with fixing their porosity remains at the optimal level and as well as after the fixation particles do not converted to mass and their dimensions are still nano. Also SEM image shows that the high volume of cavities and the special absorbent surface can increase the capability and chance of this absorbent to remove pollutants [44]. The results of SEM analysis of CDP, MCDP are shown in Figs. 2a, 2b respectively.

3.2. Effect of initial NP concentration on removal efficiency

Due to the saturation of the exchange sites by adsorption, removal efficiency was decreased when the initial NP concentration was increased so that maximum removal efficiency of NP with NP concentration 1.35 mg/L was 95% and minimum removal efficiency of NP with NP concentration 10 mg/L was 70% in synthetic samples. Increases in the concentration of NP increased adsorption capacity (q_e) [45]. The results from the effect of initial NP concentrations, the interaction of two variables (adsorbent dose and NP concentration), and their impacts on removal efficiency (R %) of NP from aqueous solutions are shown in Fig. 3.

Initial concentration of NP is one of the most important effective parameters on the removal efficiency of NP from aqueous solutions. Alaton in Turkey conducted a study in 2014 on the removal of nonylphenolpolyethoxylate by photo-Fenton and H_2O_2/UV; it was concluded that increases in NP concentration increased adsorption capacity, because there are limited adsorption sites on the surface of adsorbent. By increasing NP concentration, the adsorbent surface becomes smaller than the pollutant that should be adsorbed. This causes a reduction in the efficiency and adsorption of nonylphenol from aqueous solutions [45].

3.3. Effect of pH solution on removal efficiency

In the alkaline pH range, adsorption efficiency was decreased, because the surface charge of NP in alkaline pH is negative. The adsorption of NP is reduced in alkaline conditions because of the repulsive force between the adsorb and adsorbent. With pH = 6, maximum removal efficiency of NP was 95%. Removal efficiency was decreased by increasing pH so that removal efficiency with pH = 12 was 52% in synthetic samples. The results of tests for the effect of pH, the interaction between two variables (pH and time), and their impact on NP removal efficiency (R %) from aqueous solutions are shown in Fig. 4.

Results of this study are consistent with the results of Dulov et al. in Estonia (2013) on the photochemical degradation of nonylphenol in aqueous solutions, in which they observed the removal efficiency of NP in an alkaline pH [2,32].

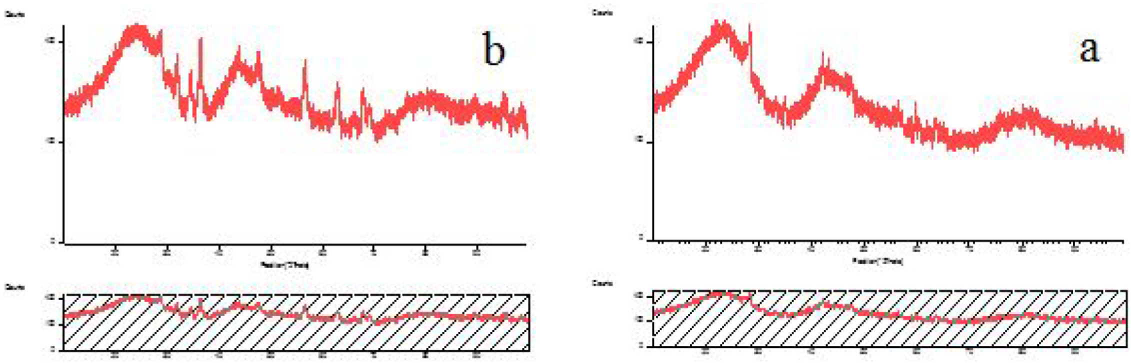


Fig. 1. Results of XRD analysis of Carbonized Date pits (a), Modified-Carbonized Date pits (b).

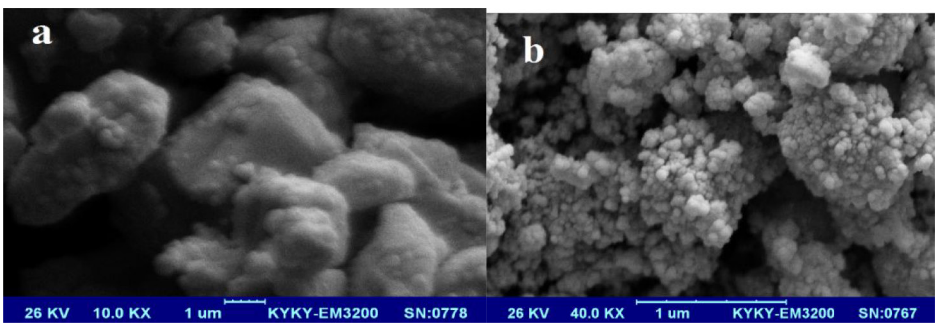


Fig. 2. Results of SEM analysis of carbonized date pits (a), fixed nanoparticles on activated carbon (b).

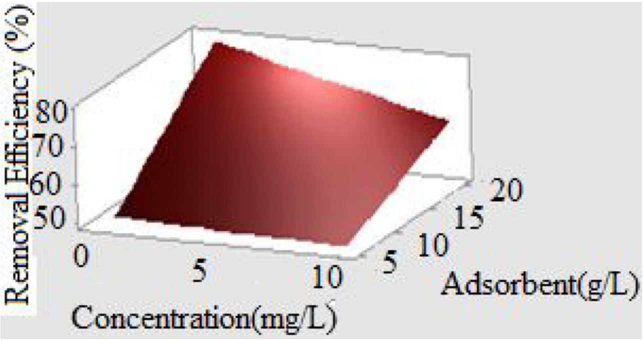


Fig. 3. Effect of initial nonylphenol concentrations, interaction of two variables (dose of adsorbent (g/L) and nonylphenol concentration (mg/L)) and their impact on removal efficiency of nonylphenol from aqueous solutions.(pH = 6 and time = 60 min).

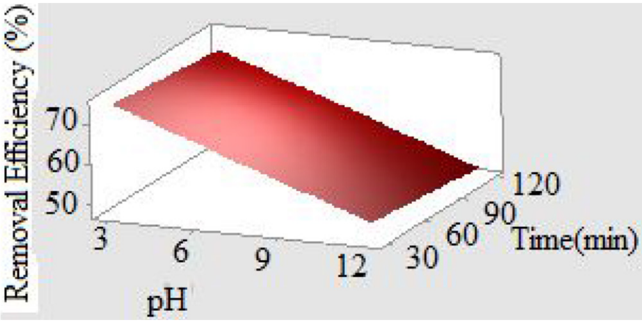


Fig. 4. Effect of pH, interaction of two variables (pH and time (min)), and their impact on removal efficiency of nonylphenol from aqueous solutions. (conc. of nonylphenol = 1.35 mg/L and adsorbent dose = 10.1 g/L).

3.4. Effect of contact time on removal efficiency

The results showed that removal efficiency increased when contact time was increased; it seems that increasing contact time is directly related to the adsorption capacity of the adsorbent so that maximum removal efficiency of NP with contact time 60 min was 95%, and minimum removal efficiency of NP with contact time 30 min was 54% in synthetic samples. The results from the effect of contact time, the interaction of two variables (dose of adsorbent and time), and their impact on removal efficiency (R%) of NP from aqueous solution are shown in Fig. 5.

There is a direct relationship between time and the removal efficiency of NP from aqueous solutions by date pits. Increasing the time reduce the NP residual concentration in the solution. The reaction was balanced within 60 min. Shuo et al. conducted a study in 2014 in China on the efficiency of nonylphenol adsorption on carbon nanotubes. They found that there was a direct relationship between removal efficiency and time [46].

3.5. Effect of adsorbent dose on removal efficiency

Considering that adsorption is a superficial process, the amount of available surface for adsorption and adsorbent mass has a significant effect on the adsorption efficiency.

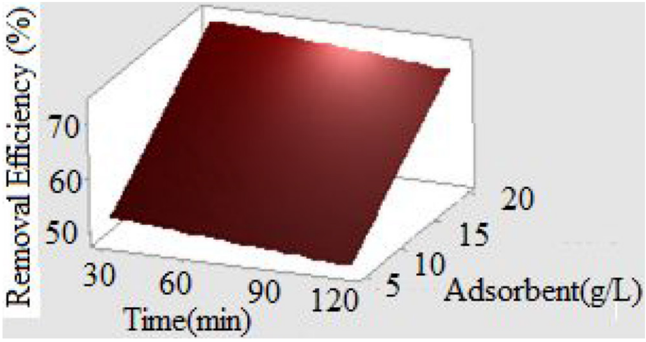


Fig. 5. Effects of contact time, interaction of two variables (dose of adsorbent (g/L) and time(min)) and their impact on removal efficiency of nonylphenol from aqueous solutions. (pH = 6 and conc. of nonylphenol = 1.35 mg/L).

Therefore, the effect of adsorbent concentration on the removal of nonylphenol was investigated [44].

NP removal efficiency has a direct relationship with changes in adsorbent dose. Increasing the adsorbent dose from 5 g/L to 10.1 g/L increased the removal efficiency from 46% to 95%. The reason is the increase in the active place of adsorption. The results regarding the effects of adsorbent dose, interaction of two variables (adsorbent dose and pH), and their impact on removal efficiency (R%) of NP from aqueous solutions are shown in Fig. 6.

Adsorbent dosage and removal efficiency are directly related in the removal of NP from aqueous solutions by MCDP. The reasons for this result are the increase in active surface sites and the increase in collisions between the adsorb and adsorbent. Similar results were achieved by Liu (2009), Tsai (2006) [1,39].

3.6. Determination of adsorption isotherms and adsorption kinetics

The Freundlich isotherm and Langmuir isotherm of NP by MCDP are shown in Figs. 7a and 7b, respectively.

Parameters of the Langmuir and Freundlich adsorption isotherm models for adsorption of nonylphenol by modified-carbonized date pits is shown in Table 3.

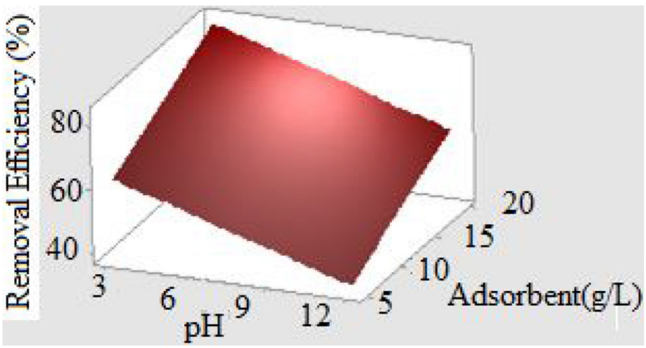


Fig. 6. Effect of adsorbent dose, the interaction of two variables (dose of adsorbent (g/L) and pH), and their impact on the removal efficiency of nonylphenol from aqueous solutions.(time = 60 min and conc. of nonylphenol = 1.35 mg/L).

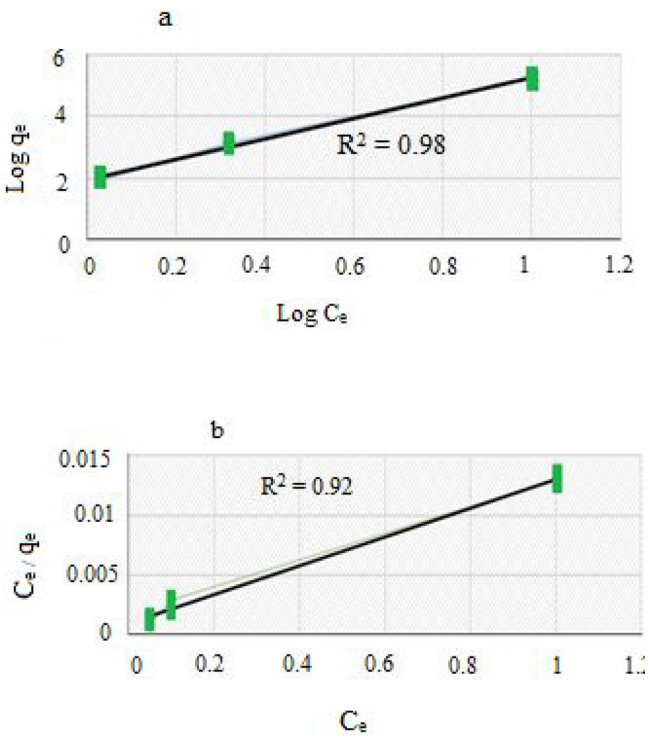


Fig. 7. Freundlich isotherm (a) and Langmuir isotherm (b) for adsorption of nonylphenol by modified-carbonized date pits.

The constants of adsorption isotherm can determine the adsorbent surface, the trend between adsorbent and pollutant, and the adsorption capacity of the pollutant. Therefore, adsorption isotherms with this important information can be useful for designing and optimizing the adsorption process [44,47,48].

Table 3
Parameters of the Langmuir and Freundlich adsorption isotherm models for adsorption of nonylphenol by modified-carbonized date pits

Langmuir			Freundlich		
Q^o (mg/g)	b (L/mg)	R^2	K_F (mg/g) (L/mg)	$1/n$	R^2
154.6	0.01	0.92	2.01	3.2	0.98

The R^2 value of the Freundlich model was 0.98 and the R^2 value of the Langmuir model was 0.92. P value of Freundlich model and Langmuir model was 0.002 and 0.008 respectively. Therefore, it can be concluded that the adsorption reaction of NP by MCDP follows the Freundlich isotherm model. As a result, it can be concluded that the adsorption of NP by MCDP is a type of multi-layer adsorption [1,49]. The value of the parameter "n" on Freundlich isotherm (which is more than 1), indicates the suitability of the adsorption of nonylphenol to activated carbon [44,50].

The pseudo-first-order model and pseudo-second-order model of NP by MCDP are shown in Fig. 8(a) and Fig. 8(b), respectively.

Information obtained about adsorption kinetics of NP by MCDP is shown in Table 4.

The R^2 of pseudo-first-order kinetics is 0.93, and the R^2 of pseudo-second-order kinetic is 0.98. P value of pseudo-second-order and pseudo-first-order was 0.001 and 0.007 respectively. Therefore, it can be concluded that the adsorption process of NP by MCDP follows the pseudo-second-order model. This issue affirms the efficiency

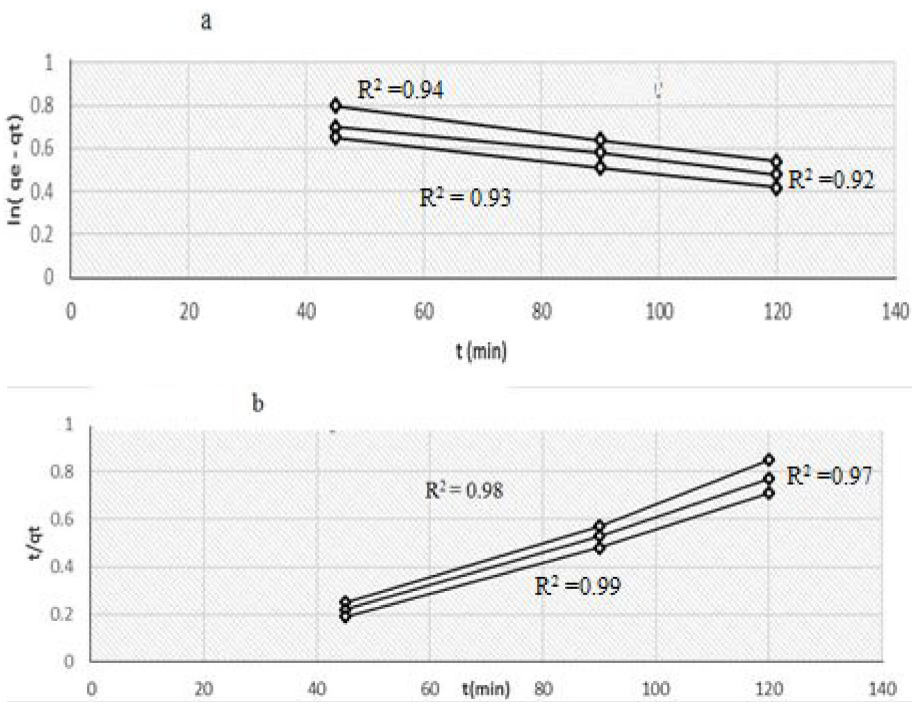


Fig. 8. Pseudo-first-order model (a) and Pseudo-second-order model (b) of nonylphenol by modified-carbonized date pits.

Table 4
Adsorption kinetic coefficients of nonylphenol by modified-carbonized date pits

Pseudo-first-order				Pseudo-second-order			
NP Concentration (mg/L)	R^2	K_2	q_e	R^2	K_1	q_e	q (Exp)
1	0.98	0.01	72.54	0.93	0.12	75.65	77.48
4	0.98	0.05	68.41	0.93	0.1	79.1	80.31
9	0.98	0.07	47.9	0.93	0.13	84.52	85.42

of adsorption at low concentrations. A reduction in initial solution concentration increases the line gradient; thus, the number of adsorbed ions is decreased. This confirms the increased adsorption efficiency in low concentrations [39,49].

3.7. Removal of NP from real wastewater

Tests of adsorption in this research were performed using synthetic solutions. After determining the optimal conditions, tests were done on wastewater from the campus of Kerman University of Medical Sciences. Primarily, its quality was determined in terms of NP, COD, TSS, NP, and pH; the results are shown in Table 5. Removal efficiency and adsorption capacity of MCDP to removal of nonylphenol have been compared with other adsorbents in Table 6.

The maximum removal efficiency and maximum adsorption capacity of NP in synthetic samples with contact time of 60 min, pH = 6, concentration of 1.35 mg/L NP, and adsorbent amount of 10.1 g/L by MCDP were 95%, 126.98 mg/g and by CDP were 65% , 86.88 mg/g respectively. Under the optimal conditions, the NP removal efficiency from wastewater from the campus of Kerman University of Medical Sciences by MCDP was 74% and by CDP was 40% respectively. There was a decrease in removal

Table 5
Physical-chemical features of wastewater from the Kerman University of Medical Sciences campus

Parameter	Amount
COD	425 (mg/L)
BOD_5	257 (mg/L)
TSS	17 (mg/L)
TDS	543 (mg/L)
TKN	75 (mg/L)
Phosphate	16.5 (mg/L)
Nitrate	16.2 (mg/L)
Sulfate	348 (mg/L)
NP	53 (mg/L)
pH	7.1

Table 6
Comparison removal efficiency and adsorption capacity of MCDP with various adsorbents to removal of the organic material removal

Entry	Adsorbents	Pollutant	Removal efficiency (%)	Adsorption capacity (mg/g)	Ref.
1	Modified-carbonized date pits by ZnO nano-particles	Bisphenol A	95	90.68	[36]
2	Magnetic molecularly imprinted polymers based on fly-ash-cenospheres	Nonylphenol		434.8	[52]
3	Membranes and activated carbon	Endocrine disruptors and pharmaceuticals	Granular activated carbon was highly effective at removing all target chemicals.	–	[51]
4	Activated carbon prepared from Populus alba	Phenol		172.41	[44]
5	Acid-treated iron-amended granular activated carbon	Bisphenol A	91–99	–	[52]
6	Activated carbons with different modification treatments (W20 and W20N)	Bisphenol A	–	382.12 and 432.34	[39]
7	Modified Red Mud	Bisphenol A	84	–	[53]
8	Modified-carbonized date pits by ZnO nano-particles	Nonylphenol	95	126.98	This work

efficiency in the real wastewater solution. This decrease in removal efficiency was caused by interferences, including the cations and anions present in the wastewater. Comparisons between adsorbents about removal efficiency NP from aqueous solutions are shown in Fig. 9.

3.8. Re usability of adsorbent

The method used in this study is reactivation, which involves heating the spent carbon in a high temperature (815ºC) furnace. The contaminants are vaporized, restoring the carbon original pore structure, allowing for its reuse [51,52]. Comparison between the number of times use of adsorbent about removal efficiency NP from aqueous solutions are shown in Fig. 10 .

4. Conclusion

Maximum removal efficiency was done by modified date pits under the optimal conditions including contact time of 60 min, pH 6, concentration of 1.35 mg/L nonylphenol, and an adsorbent amount of 10100 mg/L, were 95% for synthetic and 74% for real samples, respectively. The adsorption reaction of NP by modified date pits followed the Freundlich isotherm and pseudo-second-order kinetic models. Although carbonized date pits is a good adsorbent for the removal of NP (65%), the removal efficiency of modified-carbonized date pits (95%) is greater than that of carbonized date pits. Nanoparticles increased adsorption capacity with increases in surface area. Modified-carbonized date pits is a good adsorbent for NP because it has high efficiency, availability, re usability, high adsorption capacity; as a result, it can be recommended as a coefficient adsorbent for the removal of NP.

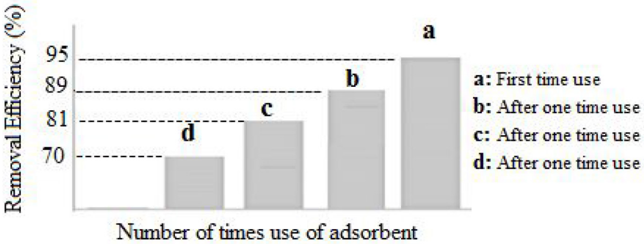


Fig. 9. Comparison between number of times use of adsorbent about removal efficiency nonylphenol from aqueous solutions.

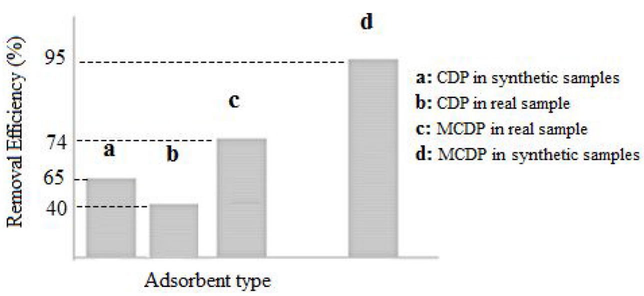


Fig. 10. Comparison between adsorbents about removal efficiency nonylphenol from aqueous solutions.

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