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Removal of bisphenol A from aqueous solutions by modified-carbonized date pits by ZnO nano-particles

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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 bisphenol A using nano-particles of zinc oxide-modified date pits. Variables examined were initial concentration of bisphenol A, contact time, pH, and adsorbent concentration. For adsorption of bisphenol A from aqueous solutions, date pits and date pits modified with nano-particles of zinc oxide were used. Adsorption isotherms and adsorption kinetics were also examined. Both adsorbents were characterized using Brunauer–Emmett–Teller and X-ray diffraction. Bisphenol A concentrations of samples were determined using ultra-high performance liquid chromatography after the adsorbents were added. Maximum removal efficiency by modified date pits under optimal conditions including contact time of 120 min, pH of 6, concentration of 1.05 mg/L bisphenol A, and an adsorbent amount of 11,000 mg/L was 95% for synthetic and 70% for real samples, respectively. The maximum adsorption capacity of bisphenol A by modified date pits under these optimal conditions was 90.68 mg/g. The adsorption reaction of bisphenol A by modified date pits followed the Freundlich isotherm and pseudo-second-order kinetic models. Modified date pits are a good adsorbent and can be recommended as an efficient adsorbent for the removal of bisphenol A.

Keywords: Bisphenol A; Date pit; Nano-particles; Design of experiment

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 group of the most hazardous pollutants 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 [2,3].

Bisphenol A (BPA; 2,2-bis(4-hydroxyphenyl)propane, 4,4′-isopropylidenediphenol), a known EDC, contains two unsaturated phenol rings and acetone [4]. Table 1 shows the structure of this material.

BPA is used in the production of epoxy resins and polycarbonate plastic, powdery colors, automatic lenses, optical windows, building materials, ophthalmic lenses, thermal paper, and other products. Due to the widespread use of this compound in many commercial and industrial products, this combination has been reported in all environmental matrices including air, water, wastewater sludge, dirt, dust, materials, food, drink, and even human samples [5]. The potential adverse effects of BPA on human health and reproductive biology can cause breast and prostate cancer, decreased sperm count, reduced fertility in men, early sexual maturation in women, nervous behavior problems, obesity, type 2 diabetes, and immunodeficiency [6].

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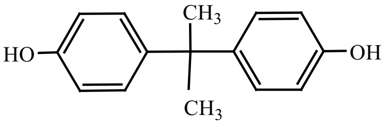
Table 1
Information on basic physical and chemical properties of BPA

Synonyms	2,2-Bis(4-hydroxyphenyl)propane; 4,4′-isopropylidenediphenol
Formula	$C_{15}H_{16}O_2$
Molecular structure of BPA	
Molecular weight	228.29 g/mol
Appearance form	Crystalline
Melting point/ freezing point	Melting point/range: 158°C–159°C(lit.)
Initial boiling point and boiling range	220°C at 5 hPa(lit.)
Odor	Odorless
Relative density	1.2 at 25°C
Water solubility	0.298 g/L at 25°C – OECD Test Guideline 105 – soluble

The maximum concentrations of BPA were obtained as approximately 17.2 mg/L in the contaminated landfill leachate, 12 µg/L in flow water, and 0.1 µg/L in drinking water [7]. Limits of BPA in surface water have been reported as 1,000–15,000 µg/L [3]. Unfortunately, due to the complex molecular structures of aromatics and their low ability for biodegradation, the complete removal of BPA is not possible [8]. Among treatment methods, the efficacy of biological methods is not satisfactory because of the high toxicity of BPA for aerobic and anaerobic bacteria [9]. Ultrafiltration and reverse osmosis methods have high operating costs and thus are not economic [10].

As a result, more advanced treatment processes are required for the removal of BPA. Many different methods have been used to remove this material, including advanced oxidation methods such as Fenton and electro Fenton [11], ozonation with ultraviolet light [12], use of catalysts [13], and adsorption methods using adsorbents such as activated carbon, chitosan, and nano-particles [14,15]. The adsorption process is a priority because of its lower initial cost, simplicity of operation, lack of harmful secondary pollutants production, low sensitivity to stream fluctuations, the ineffectiveness of toxic chemicals in the process, and 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 [16]. The use of ash as a low-cost adsorbent for the removal of phenolic compounds is recommended [17]. Its low cost makes it a good alternative for activated carbon. Other materials have been studied as low-cost adsorbents. One of these bioadsorbents is the date pit. Some bioadsorbents have been studied for use in removing contaminants from aquatic environments, including bark, sawdust, chitosan, wheat, rice, and reed [17].

Studies show that carbon produced from date pits has a remarkable ability to adsorb contaminants. Ash produced from date pits has been used to adsorb gases such as methane, nitrogen, ethane, ethylene, and remove heavy metals such as ions of cadmium (Cd^{2+}) and copper ions (Cu^{2+}), remove various colors such as methylene blue, and reduce COD, BOD, and TOC in water and sanitation, and has achieved significant results [18–20]. The use of nano-particles to improve the performance of adsorbents has been considered, including the use of iron and carbide nano-particles on carbon to remove arsenic [21].

Liu et al. [7] studied the adsorption of BPA from aqueous solutions on activated carbon with different modification methods. Huling et al. [37] studied the effect of temperature on the adsorption and oxidation degradation of BPA in granular activated carbon modified with iron in acidic conditions. Iravani et al. [40] surveyed the removal of BPA from aqueous solutions by single-walled carbon nanotubes. Yang et al. [4] investigated the advanced removal of BPA from aqueous solutions by modified montmorillonite without a cationic surfactant. Malakootian et al. [22], Mehdizadeh and Malakootian [23], Asadi and Malakootian [24], Jafari-Mansoorian et al. [25], and Mansuri and Malakootian [26] conducted extensive research using different methods to study phenol and its derivatives.

According to scientific sources, no study has been done in the field of BPA adsorption using modified-carbonized date pits by ZnO nano-particles (MCDP).

2. Experiments

2.1. Materials

BPA (99% purity) and ZnO nano-particles (40 nm) were purchased from Sigma-Aldrich (USA). 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 (Bam, Kerman, Iran). Information on basic physical and chemical properties of BPA is summarized in Table 1.

2.2. Analytical methods

The pH of solutions was measured by pH meter (model: Hanna). Magnetic stirrer (model: Fan Azma Gostar) was used for stirring. Scale (model: Shimadzu-Libror) was used to weigh chemicals.

2.3. Experimental practices

This experimental research was ended in January 2017 at the Environmental Health Engineering Research Center of Kerman University of Medical Sciences.

First, the BPA stock solution (1,000 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 25°C. To prepare the stock solution, BPA was first dissolved in 2 mL ethanol 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 4°C [4,7].

After adding the required amount of adsorbent to each sample, the adsorbent and BPA were thoroughly mixed using a magnetic stirrer at a speed of 250 rpm. Adsorbent was separated from samples using centrifuges at a speed of 1,400 rpm for 15 min. Then the samples were passed through filter paper with a pore size of 0.45 μm. Sample concentrations of BPA were determined using a ultra-high performance liquid chromatography device (AZURA model, KNAUER, Germany) under the following conditions:

Column: Ascentis Express C_{18}, 10 cm × 2.1 mm I.D., 2.7; mobile phase: water:acetonitrile (60:40); flow rate: 0.4 mL/min; pressure: 3,268 psi (225 bar); column temperature: 35°C; detector: UV (230 nm); injection: 1 μL.

The adsorption capacity and removal percentage of BPA onto adsorbent were obtained according to Eqs. (1) and (2):

$$q_e = \left(C_0 - C_e / m\right) \times V \tag{1}$$

$$\%R = \left[(C_0 - C_e\right) / C_0] \times 100 \tag{2}$$

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

2.4. 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 100°C for 24 h to remove moisture. The dried kernels were ground with a powder mill. To stabilize the nano-particles on the adsorbent, the immersion method was used; 500 mL of double-distilled water was poured into a flask and 1 g of nano-particles 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 100°C for 24 h to remove its moisture. The dried powder was placed in an electric furnace at 700°C for 2 h to stabilize the nano-particles on the adsorbent and to prepare the adsorbent [27].

2.5. Characterization methods

To measure the porosity of the surface area adsorbents, the Brunauer–Emmett–Teller (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.

2.6. Adsorption isotherms

Two isotherm equations were used to determine the Langmuir and Freundlich models:

$$C_e / q_e = \left(1 / Q^\circ b\right) + \left(C_e / Q^\circ\right) \tag{3}$$

$$\log\left(q_e\right) = \log\left(K_F\right) + 1 / n \log\left(C_e\right) \tag{4}$$

where C_e and q_e, respectively, are equilibrium concentration and equilibrium adsorption capacity (mg/g), $Q°$ is maximum equilibrium adsorption capacity of BPA 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.

2.7. Adsorption kinetics

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. (5) and (6), respectively:

$$\log\left(q - q_e\right) = \log\left(q_e\right) - K_1.t / 2.303 \tag{5}$$

$$t / q_t = 1 / K_2 q_e{}^2 + t / q_e \tag{6}$$

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

2.8. Design of experiments

Screening tests were performed using the software Minitab 17. Then the removal of BPA was optimized using the response surface method with the Box-Behnken model. Data analysis was performed using Minitab 17 and Excel 2013. To prevent systemic errors, experiments were performed in random order with three replicates [28].

2.9. Real solution

Tests of adsorption in this research were performed using synthetic solutions. After determining optimal conditions, tests were done on wastewater from the campus of Kerman University of Medical Sciences. Primarily, its quality was determined in terms of BOD_5, COD, TSS, BPA, and pH and is shown in Table 2.

2.10. Effective parameters on removal efficiency

This study examined the parameters affecting removal efficiency, including pH, contact time, initial BPA concentration, and adsorbent concentration that the values are shown in Table 3.

3. Results and discussions

3.1. Effect of initial BPA concentration on removal efficiency

Due to the saturation of the exchange sites by adsorption, removal efficiency was decreased when the initial BPA concentration was increased. At the first exchange sites the amount of BPA removed was increased, but with a decrease in the exchange site, adsorption efficiency was decreased [1,29]. When BPA concentration was increased, adsorption capacity (q_e) also increased [3]. The results from the effect of initial BPA concentrations, the interaction of two variables

Table 2
Physical–chemical features of wastewater – from 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)
BPA	45 (mg/L)
pH	7.1

Table 3
Effective parameters on removal efficiency of BPA from aqueous solutions

Parameter	Amount
pH	3–11
Contact time	30–120 min
BPA concentration	1–20 mg/L
Adsorbent concentration	5,000–20,000 mg/L

(dose of adsorbent and BPA concentration), and their impacts on BPA removal efficiency from aqueous solutions are shown in Fig. 1.

The initial concentration of BPA is one of the most important parameters affecting the removal of BPA from aqueous solutions. By increasing the initial BPA concentration, the adsorption capacity also increased. Tsai et al. [30] compared modified carbon nanotubes for the removal of BPA and also achieved this result. It is for this reason that the adsorbent has limited adsorbed sites. When the concentration of BPA is increased, the available levels of adsorbent are less. The result was reduced efficiency and the adsorption of BPA from aqueous solutions [3].

3.2. Effect of pH solution on removal efficiency

Removal efficiency was increased by increasing pH from 3 to 8.2; at pH values higher than 8.2 to 11, efficiency was reduced. In the alkaline pH range, adsorption efficiency was decreased [31,32]. Because surface charge of BPA in alkaline pH is negative and finally reducing adsorption of BPA in alkaline conditions because of the repulsive force between the adsorbate and adsorbent [3]. The results of tests for the effect of pH, the interaction between two variables (pH and time), and their impact on BPA removal efficiency from aqueous solutions are shown in Fig. 2.

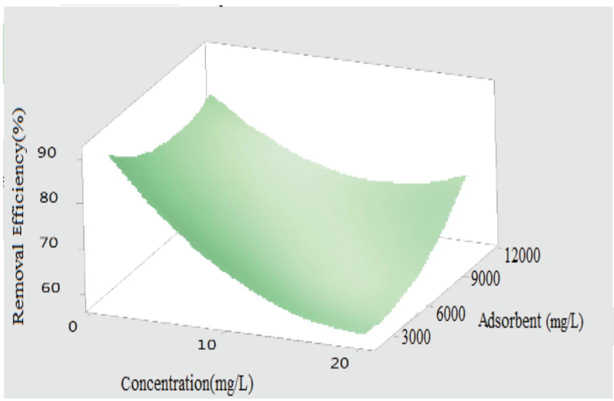


Fig. 1. Effect of initial BPA concentrations, interaction of two variables (dose of adsorbent [mg/L] and BPA concentration [mg/L]) and their impact on removal efficiency of BPA from aqueous solutions (pH = 6 and time = 120 min).

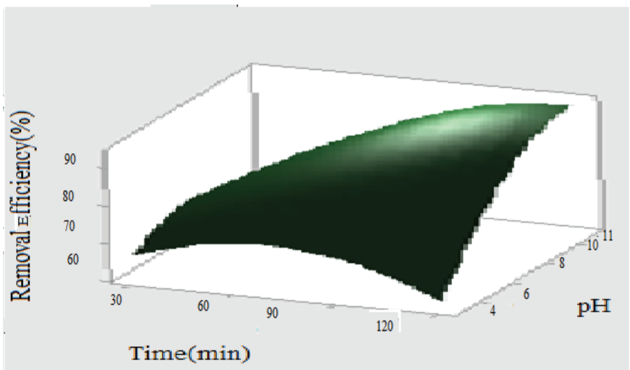


Fig. 2. Effect of pH, interaction of two variables (pH and time [min]), and their impact on removal efficiency of BPA from aqueous solutions (concentration of BPA = 1.05 mg/L and adsorbent dose = 11,000 mg/L).

At the higher pH 8, removal efficiency of BPA by MCDP was decreased. The surface charge of BPA at alkaline pH is negative, thus the adsorption of BPA in alkaline conditions is reduced because of the repulsive force between the adsorbate and adsorbent. The results of this study were consistent with the results of a study by Joseph et al. [34] conducted which investigated the adsorption of BPA and estradiol 17 α – ethynyl. They observed a reduction in the removal efficiency of BPA at pH values higher than 9 [33].

3.3. Effect of contact time on removal efficiency

The results showed that removal efficiency increased when contact time was increased and that increasing contact time is directly related to the adsorption capacity of the adsorbent [2,4,34]. The results from the effect of contact time, the interaction of two variables (dose of adsorbent and time), and their impact on removal efficiency of BPA from aqueous solution are shown in Fig. 3.

With increase in contact time, the remaining BPA concentration in the solution was reduced. Contact time to reach equilibrium was 120 min. Samadi et al. [3] studied the performance of multi-walled nanotube carbon in removing BPA from aqueous environments. They found that contact time and removal efficiency have a direct relationship, and equilibrium contact time was 60 min. This short time balance is because adsorption was done on the superficial layers of the adsorbent which probably caused the lack of adsorption of BPA and shortened the time balance.

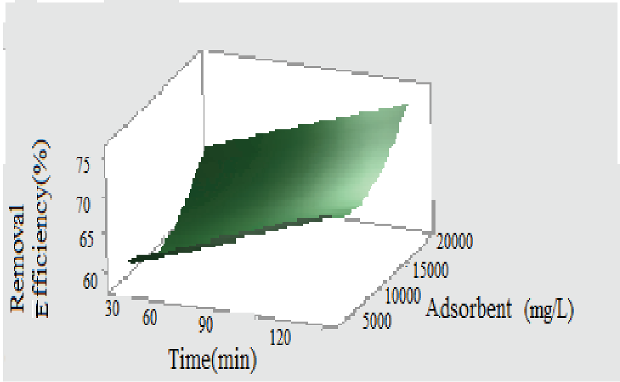


Fig. 3. Effects of contact time, interaction of two variables (dose of adsorbent (mg/L), and time [min]) and their impact on removal efficiency of BPA from aqueous solutions (pH = 6 and concentration of BPA = 1.05 mg/L).

3.4. Effect of adsorbent concentration on removal efficiency

Results showed that the removal efficiency of BPA was directly related to changes in the adsorbent concentration by increasing the adsorbent concentration from 5,000 to 20,000 mg/L. The results regarding the effects of adsorbent dose, interaction of two variables (dose of adsorbent and pH), and their impact on removal efficiency of BPA from aqueous solutions are shown in Fig. 4.

The adsorbent concentration and removal efficiency are directly related to the removal of BPA from aqueous solutions by MCDP. The removal efficiency was increased from 44% to 95% because of the increased adsorption surface active sites. The reasons for this result are the increase in active surface sites and the increase in collisions between the adsorbate and the adsorbent. When adsorbent concentration was increased, adsorption capacity (q_e) was decreased [3]. Similar results were achieved by Liu et al. [7], Tien Tsai [1], Samadi et al. [3], Shokohi et al. [35], and Shahryari et al. [36].

3.5. 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 4.

XRD test was performed and confirmed the modifying of the adsorbent well. As shown in Fig. 6, new peaks were appeared in the graph after modifying the adsorbent that proved the presence of zinc oxide nano-particles on the surface. The results of XRD analysis of CDP, MCDP, and ZnO nano-particles are shown in Figs. 5(a)–(c), respectively.

3.6. Determination of adsorption isotherms

The Freundlich isotherm and Langmuir isotherm of BPA by MCDP are shown in Figs. 6(a) and (b).

Balance information obtained from BPA adsorption by MCDP is shown in Table 5.

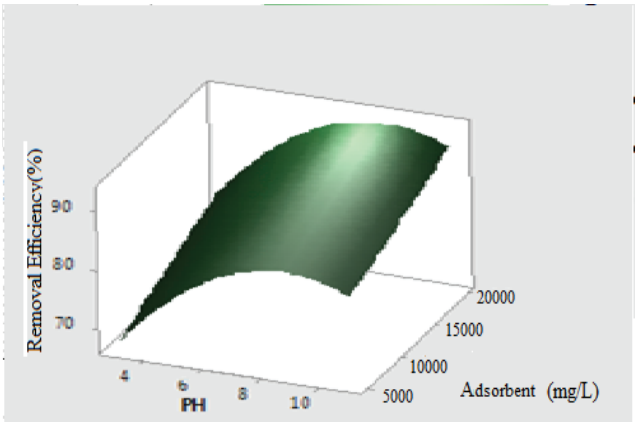


Fig. 4. Effect of adsorbent dose, the interaction of two variables (dose of adsorbent [mg/L] and pH), and their impact on the removal efficiency of BPA from aqueous solutions (time = 120 min and concentration of BPA = 1.05 mg/L).

Table 4
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	
t-Plot micropore volume	0.03 cm³/g
Pore size	
Adsorption average pore diameter (4V/A by BET)	1.57 nm

The R^2 value of the Freundlich model was 0.99, and the R^2 value of the Langmuir model was 0.98. p-value of Freundlich model and Langmuir model was 0.001 and 0.004, respectively. Therefore, it can be concluded that the adsorption reaction of BPA by MCDP follows the Freundlich isotherm model. As a result, it can be concluded that the adsorption of BPA by MCDP is a type of multi-layer adsorption [3,31,32].

3.7. Determination of adsorption kinetics

The pseudo-first-order model and pseudo-second-order model of BPA by MCDP are shown in Figs. 7(a) and (b).

Information obtained about adsorption kinetics of BPA by MCDP is shown in Table 6.

The R^2 of the pseudo-first-order model was 0.98, and the R^2 of the pseudo-second-order model was 0.99. p-value of pseudo-second-order and pseudo-first-order was 0.003 and 0.005, respectively. Therefore, it can be concluded that the adsorption reaction of BPA by MCDP follows the pseudo-second-order model. This issue affirms the efficiency of adsorption at low concentrations [7,32]. Adsorption experiments were performed using synthetic solutions and at optimal conditions for real wastewater. MCDP efficiency in the

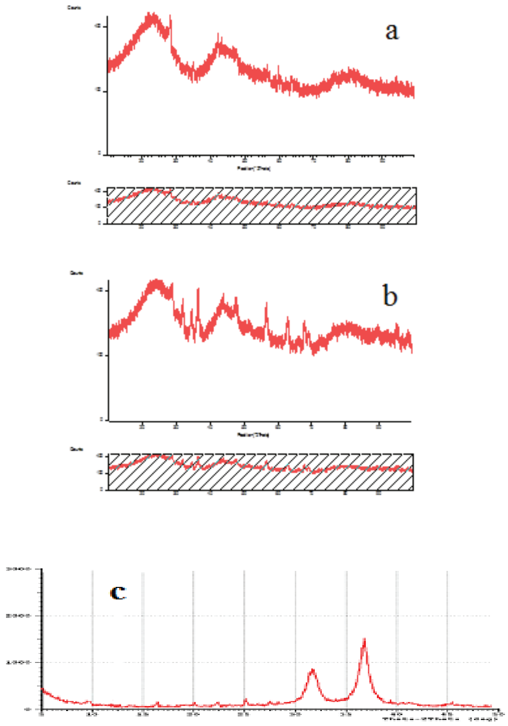


Fig. 5. Results of XRD analysis of CDP (a), MCDP (b), and ZnO nano-particles (c).

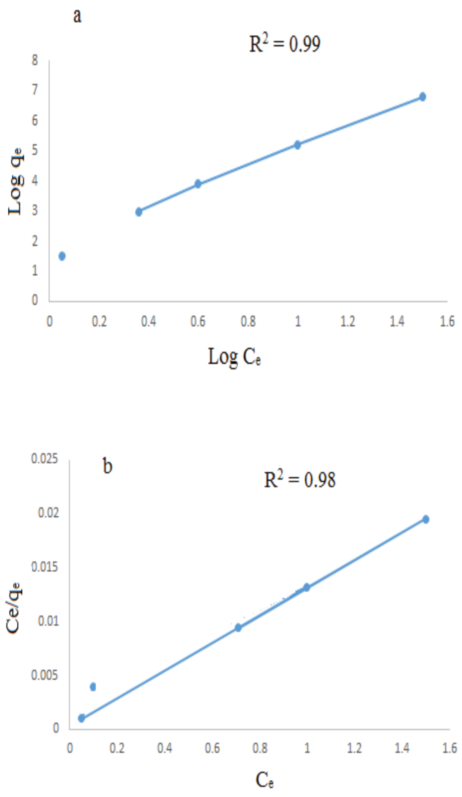


Fig. 6. Freundlich isotherm (a) and Langmuir isotherm (b) for adsorption of BPA by MCDP.

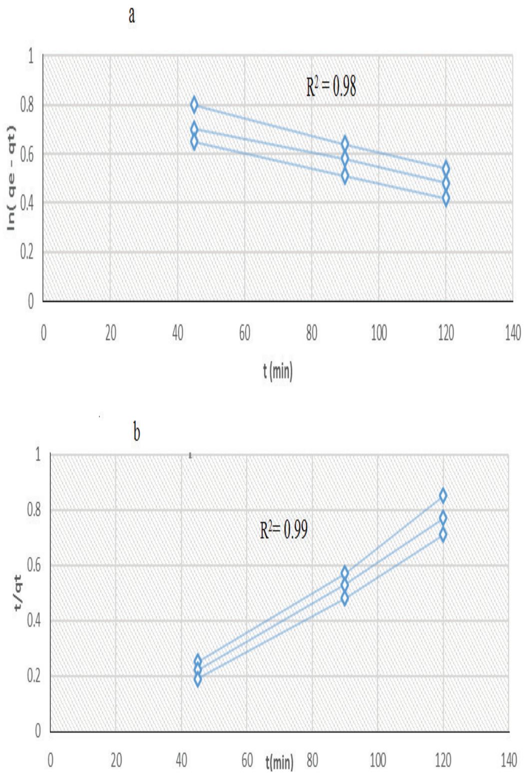


Fig. 7. Pseudo-first-order model (a) and pseudo-second-order model (b) of BPA by MCDP.

Table 5
Parameters of the Langmuir and Freundlich adsorption isotherm models for adsorption of BPA by MCDP

Langmuir			Freundlich		
$Q°$ (mg/g)	b (L/mg)	R^2	K_F (mg/g) (L/mg)	$1/n$ (–)	R^2
166.6	0.01	0.98	2.02	3.31	0.99

removal of BPA from real wastewater was lower in the actual samples (70%) than in the synthetic samples (95%).

3.8. Removal of BPA from real wastewater

The maximum removal efficiency and maximum adsorption capacity of BPA by MCDP with a contact time of 120 min, pH 6, BPA concentration 1.05 mg/L and adsorbent in the amount of 11,000 mg/L were 95% and 90.68 mg/g, respectively. The maximum removal efficiency and maximum adsorption capacity of BPA by CDP on synthetic samples were reported as 60% and 66.81 mg/g, respectively. The BPA removal efficiency under optimal conditions of wastewater from the campus of Kerman University of Medical Sciences was reported 70%. There was a decrease in removal efficiency in the real wastewater solution. This decrease in removal efficiency was caused by interferences, including the cations and anions present in the wastewater. Removal efficiency and adsorption capacity of MCDP to removal of BPA have been compared with other adsorbents in Table 7.

Table 6
Adsorption kinetic coefficients of BPA by MCDP

Pseudo-second-order				Pseudo-first-order			
BPA concentration (mg/L)	R^2	K_2	q_e	R^2	K_1	q_e	q (exp)
1.05	0.99	0.02	84.32	0.98	0.13	85.89	88.98
5	0.99	0.06	65.36	0.98	0.11	89.7	90.21
10	0.99	0.08	48.96	0.97	0.12	90.68	92.63

Table 7
Comparison of removal efficiency and adsorption capacity of MCDP with various adsorbents to removal of bisphenol A

Entry	Adsorbents	Pollutant	Removal efficiency (%)	Adsorption capacity (mg/g)	Reference
1	Acid-treated iron-amended granular activated carbon	Bisphenol A	91–99	–	[37]
2	Activated carbons with different modification treatments (W20 and W20N)	Bisphenol A	–	382.12 and 432.34	[38]
3	Modified red mud	Bisphenol A	84	–	[39]
4	Single-walled carbon nanotubes	Bisphenol A	–	71.42	[40]
5	Organomontmorillonites modified with novel Gemini pyridinium surfactants containing long alkyl chain	Bisphenol A	–	222.20	[4]
6	Modified-carbonized date pits by ZnO nano-particles	Bisphenol A	95	90.68	This work

4. Conclusion

Maximum removal efficiency by modified date pits under optimal conditions including contact time of 120 min, pH of 6, concentration of 1.05 mg/L bisphenol A, and an adsorbent amount of 11,000 mg/L were 95% for synthetic and 70% for real samples, respectively. The adsorption reaction of bisphenol A by modified date pits followed the Freundlich isotherm and pseudo-second-order kinetic models. Modified date pits are a good adsorbent and can be recommended as a coefficient adsorbent for the removal of bisphenol A.

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