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A Study of Isotherms and Adsorption Kinetic of Di (2-Ethylhexyl) Phthalate by Nano Cellulose from Aqueous Solutions

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ABSTRACT

Introduction: Di (2-ethylhexyl) phthalate is one of the most abundant phthalate esters and it is widely used as softeners in plastic products. Malformation, carcinogenicity, the poisoning of the reproductive system, and also the disruption of the human endocrine system are the harmful effects of these substances.

Materials and Methods: In this research, the removal of di (2-ethylhexyl) phthalate from aqueous solutions by cellulose nanofiber non-continuous was studied. The effects of some variables such as the initial concentration of the di (2-ethylhexyl) phthalate, the adsorbent dosage, the contact time, and the pH at room temperature were tested. The pseudo-first-order and pseudo-second-order kinetic models were used to describe the kinetic data. furthermore, the Freundlich and Langmuir adsorption models were tested based on the optimum conditions.

Results: The results indicated that the adsorption of di (2-ethylhexyl) phthalate follows the pseudo-second-order kinetic model (R^2 = 0.9674) and the Langmuir isotherm (R^2 = 0.9573).

Conclusion: Due to the high adsorption capacity of the cellulose nano fiber (312.5 mg/gr), it can be concluded that it is an appropriate adsorbent for removal of di (2-ethylhexyl) phthalate from aqueous solutions.

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Introduction

Phthalic acid esters or phthalate esters (PAEs) are chemically stable, liquid, without taste, colorless, and odorless in a wide range of temperatures and are water-soluble. Some of the properties of this group of substances are low degradability, very low aqueous solubility, and high hydrophobicity [1, 2]. The global production of

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these substances is approximately 6 million tons per year [3]. Di (2-ethylhexyl) phthalate is one of the most abundant phthalate esters. Recently, they have found wide use as softeners in plastic products such as polyvinyl chloride (PVC) [4]. These substances, due to their low cost, flexibility, durability, and the stability of final products as well as their excellent physical properties, are used in medical devices, cosmetics, clothing, food packaging, building materials, flooring materials, wiring, and plastic tubes in toys [3, 5, 6]. The United States of America Environmental Protection Agency (USEPA) has classified di (2-ethylhexyl) phthalate as a possible carcinogen to humans and a primary pollutant for the environment [7, 8]. Some of its effects are malformation, carcinogenicity, disruption of the human endocrine system and anti-androgenic effects while it has also been found to poison the reproductive and growth systems in laboratory mice [4, 9, 10]. The World Health Organization (WHO) has announced the maximum acceptable concentration of di (2-ethylhexyl) phthalate to be equal to 0.008 mg/L in drinking water [11].

Since these substances are used in a wide range of industrial and commercial applications, and because these substances do not bond polymers chemically, they are gradually released during the making, the application and also, the final disposal of the products. There is strong evidence indicating they should be removed from the environment [3, 12, 13]. Some of the removal methods include: 1) Removal by microorganisms, but given that di (2-etylhexyl) phthalate is a long-chain phthalate, a long time is needed for their decomposition, which renders this method ineffective. 2) Advanced oxidation processes, though they entail a high cost of use. 3) Physical and chemical methods[3].

Meanwhile, the adsorption process is considered more widely due to certain advantages such as simplicity, low cost and cost-effectiveness, high efficiency, minimizing chemicals or biological sludge, the capability of reviving bio-adsorbents [13, 14]. Wood is one of the substances with cellulose in its structure. Cellulose is a linear polymer and one of the most organic materials with an annual global production of about 1.5 million tons. Cellulose is considered to be both eco-friendly substance and renewable [15, 16]. Cellulose Nano Fibers (CNFs) is a unique nanosized substance which can be extracted in various ways from the plants that contain substances like lignocellulose. These substances are considered due to characteristics like low density, low cost, and good mechanical properties [17]. Several studies have been conducted until now in the field of the efficiency of effective adsorbents based on cellulosic materials in removing pollutants. In this field, the research of Azadbakht et al. can be especially mentioned for having removed nitrate from aqueous solutions through nanocrystalline cellulose [18]. In the same field, Samiyeh et al. succeeded in removing Janus Green B and Methylene Blue from aqueous solutions through nanocrystalline cellulose [19]. Mohan et al. removed diethyl phthalate from aqueous solutions through activated carbon as adsorbent [20]. In another research, Ziapoor et al. succeeded in removing Acid Orange 7 from aqueous solutions with the use of soy as an adsorbent [21]. In another evaluation, Zarean et al. attempted to remove di (2-ethylhexyl) phthalate by advanced oxidation processes and they reported that the study was successful [22].

This research evaluates the process of di (2-ethylhexyl) phthalate removal with the cellulose nano-fiber extracted from softwood used as an adsorbent, through the kinetic and adsorption isotherm models.

Materials and Methods

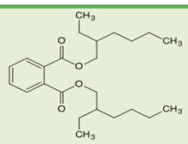
Variables in this study include the pollutant concentrations of di (2-ethylhexyl) phthalate to be 1, 2, 5, 10 mg/L (this range has been selected based on previous studies) [23], adsorbent dosages of 0.5, 1, 2, 3 gr/L, contact time of 30, 60, 120, 180 minutes, and pH 3, 5, 7, 9 (this range has been selected based on previous studies) [24, 25]

Preparing the Synthetic Solutions

This research is an experimental-laboratory study which was conducted non-continuous in the laboratory of the Faculty of Health, Isfahan University of Medical Sciences.

First, the stock solution of di (2-ethylhexyl) phthalate was bought from Merck, Germany, and its physiochemical properties have been provided in Table 1. It was prepared with the concentration of 1000 mg/L and then, the required solutions were made daily from the stock solution. In all stages of the test, the volume of the used solution was considered to be 100 ml. To adjust the pH of the solutions, 0.1 molar sodium hydroxide and 0.1 molar hydrochloric acid were used.

Table 1: The physicochemical properties of di (2-ethylhexyl) phthalate

Water solubility (gr/L)at 25 ºC	Molecular weight (gr/mol)	Formula	Structure	Compound
0.001 <	390.56	$C_{24}H_{38}O_4$		DEHP

Conducting the Tests in Discontinuous Conditions

The adsorption tests were conducted in a glass bottle with 110 ml capacity as the adsorption reactor. The adsorbent dosage with concentrations of 1, 2, 5, and 10 mg/L with pH levels of 3, 5, 7, and 9 were placed on a shaker with 250 rounds per minute for 30, 60, 120, and 180 minutes to make an effective contact between the adsorbent and the pollutant solution. After this, the solution was passed through Whatman filter paper of 0.45 micrometers thickness and connected to a gas chromatograph (GC) (7890A, model MSD, Agilent). In this mode, the temperature of the location of injecting the sample and the temperature of the detector were selected to be 250ºC and 280ºC, respectively, with a split mode in discharge of 1 ml/min. The oven temperature program was set in this way: 100ºC for three minutes, then, an increase to 210ºC with a velocity of 10ºC/min, a subsequent increase of the temperature to 250ºC with a velocity of 5ºC/min and finally, the increase of the temperature to 280ºC with a velocity of 30ºC/min for 4 minutes. Helium was used as the carrier gas. The volume of the sample harvested, in order to inject to the apparatus, was 3 µl.

The equations of the removal efficiency and the value of di (2-ethylhexyl) phthalate adsorbed at the balance time are, respectively, the following:

$$\%\ Removal = \frac{(c_0 - c_t)}{c_0} \times 100$$

$$q = \frac{(c_0 - c_t)v}{w}$$

In these equations:

The q is the adsorption capacity in mg/gr, C_0 and C_t are the initial concentration of di (2-ethylhexyl) phthalate and its concentration after t time in mg/L, v is the volume of the aqueous solution in L, and w is the adsorbent mass in grams.

Preparing the Adsorbent

The adsorbent of cellulose nanofiber extracted from the softwood purchased from Nano Novin Polymer Co. in Mazandaran was used in order to adsorb di (2-ethylhexyl) phthalate; its properties are described in Table 2. Since the used adsorbent is 2.5 percent gel; it was centrifuged two times with 10000 rounds per minute to remove its additional water.

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Table 2: The properties of the adsorbent evaluated in this research

Characteristic of nano fiber	
Chemical formula	$(C_5H_{10}O_5)n$
Status	Gel 2.5%
Color	White
Generation method	Mechanical
Diameter	Average 35 nm
Purity	99% <

The results of measuring the morphology of the adsorbent sample of cellulose nanofiber through field emission scanning electron microscopy growth (FESEM) have been shown in Figure 1.

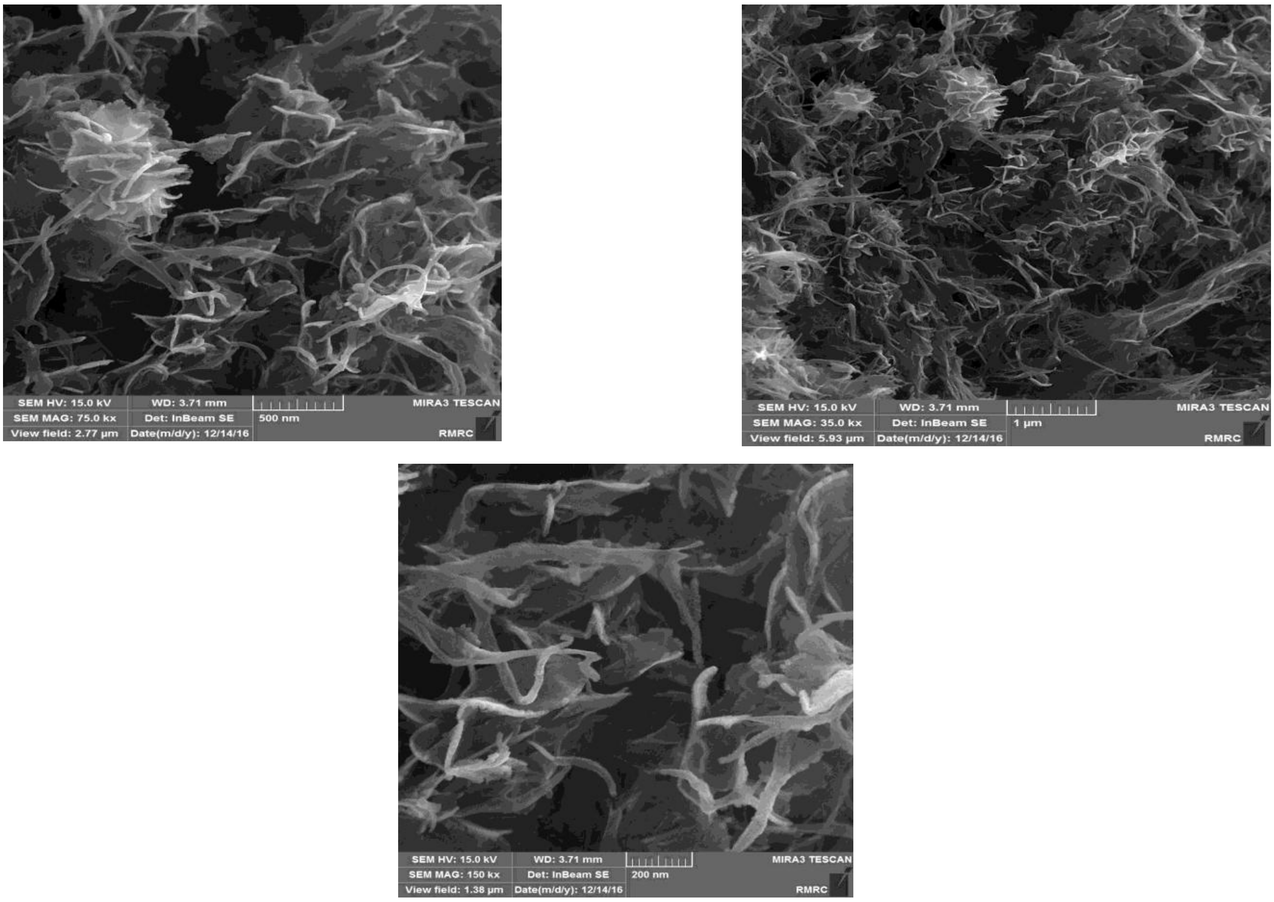

Figure 1: The images of field emission scanning electron microscopy growth (FESEM) of the cellulose nanofiber

The Equilibrium Models (Adsorption Isotherm)

The tests required to evaluate the adsorption isotherm with selecting the basis conditions are as following:

The optimum value of 0.5 gr/L of the studied adsorbent was added to 100 ml of the solution with concentrations of 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 mg/L. Then, it was placed on a shaker for an optimum time of 30 minutes with a velocity of 250 rounds per minute. After this, the solution was passed through 0.45 micrometers Whatman filter paper. In this research, the Freundlich and Langmuir models were used in order to evaluate the adsorption model and the adsorption capacity. The linear equations of the Freundlich and Langmuir models to determine the adsorption capacity are as following.

The linear form of the Freundlich adsorption model:

$$\log q_e = \log k_f + \frac{1}{n} \log c_e$$

The linear form of the Langmuir adsorption model:

$$\frac{c_e}{q_e} = \frac{c_e}{q_m} + \frac{1}{b} . \frac{1}{q_m}$$

In these equations,

C_e is the concentration of the pollutant substance in equilibrium in mg/L, q_e is the amount of the pollutant adsorbed in the adsorbent mass unit in mg/gr, k_f and n are the equilibrium constants of Freundlich which, respectively, indicate the bond strength of the adsorbent and the bond energies between the pollutant and the adsorbent, q_m is the adsorption capacity measured under laboratory conditions in mg/gr, b is the equilibrium constant of Langmuir depending on the adsorption energy in 1 per mg. A dimensionless constant, termed the isolation parameter (R_L), is used for favorability or unfavorability of the adsorption system; the equation of that is as following:

$$R_L = \frac{1}{1 + bc_0}$$

In this equation, C_0 is the initial concentration of di (2-ethylhexyl) phthalate in mg/L, b is the equilibrium constant of Langmuir in one per mg. Table 3 indicates the type of the adsorption isotherm in terms of favorability or unfavorability.

Table 3: The effect of isolation parameters on the type of the adsorption isotherm

Separation factor	Types of isotherms
$R_L > 1$	Unfavorable
$< R_L < 1$	Favorable
$R_L = 1$	Linear
$R_L = 0$	Irreversible

Non-Equilibrium Models (Adsorption Kinetic)

For the adsorption kinetic tests, 0.5 gr/L of the studied adsorbent was added to 100 ml of the solution with the optimum concentration of 10 mg/L and the optimum value of pH equal to 7. Then, it was placed on a shaker with 250 rounds per minute for 30, 90, 120, and 180 minutes. After this, the solution was passed through a 0.45 micrometer Whatman filter. Then, the pseudo-first-order and the pseudo-second-order absorption kinetic models were used to describe the data, the linear forms of the mentioned equations are the following:

The linear form of the pseudo-first-order equation:

$$ln(q_e - q_t) = lnq_e - k_1 t$$

The linear form of the pseudo-second-order equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

q_e is value of the adsorbed component (di (2-ethylhexyl) phthalate) at equilibrium (mg/g), q_t is value of the adsorbed component in t time, k_1 (1/min) and k_2 (g/mg.min) are the equilibrium constants of velocities of the pseudo-first-order and the pseudo-second-order kinetic equations, respectively.

Ethical approval

This research was approved by Isfahan University of Medical Sciences (Code: IR.MUI.REC.1394.3.910).The authors hereby certify that all data collected during the study are the same as stated in this manuscript and no data from the study has been or will be published elsewhere.

Results

Determining the Optimum Conditions

The optimum conditions for the adsorption of di (2-ethylhexyl) phthalate by cellulose nanofiber were obtained through the pollutant concentration equal to 10 mg/L, the adsorbent dosage equal to 0.5 gr/L, contact time equal to 30 minutes, and pH = 7.

Adsorption Isotherms

The Freundlich and Langmuir models were used, as shown in Figures 2 and 3, in order to

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analyze the data. The adsorption coefficients and constants of the Freundlich and Langmuir isotherm models have been listed in Table 4. The maximum adsorption capacity (q_m) is 312.5 mg/gr. furthermore, due to the higher correlation coefficient (R^2) for the Langmuir model (0.9573) compared to the Freundlich model (0.949), the Langmuir isotherm is a better model for the adsorption of di (2-ethylhexyl) phthalate by cellulose nanofiber.

Table 4: The coefficients and the constants of the Freundlich and Langmuir isotherm models

Langmuir isotherm			Freundlich isotherm		
R^2	b (1/mg)	q_{max}	R^2	n	k_f
0.96	0.18	312.5	0.95	0.51	67.93

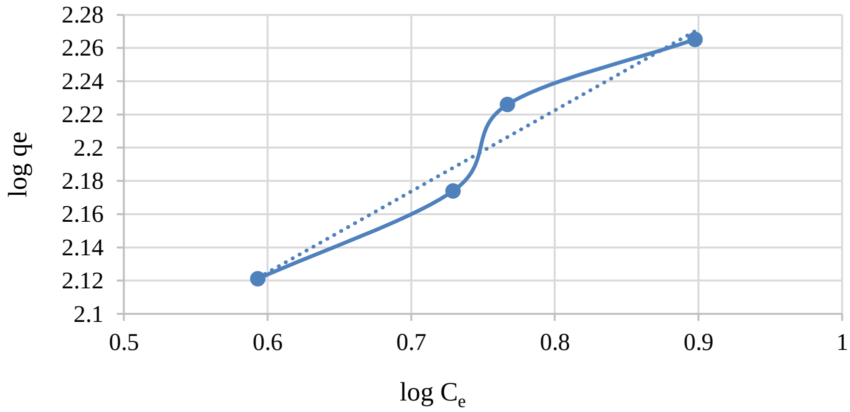

Figure 2: The Freundlich isotherm for the adsorption of di (2-ethylhexyl) phthalate by cellulose nanofiber for the adsorbent dosage equal to 0.5 gr/L, contact time equal to 30 minutes, and pH = 7

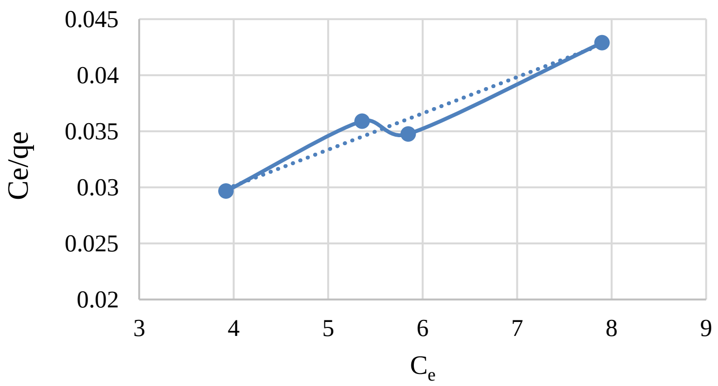

Figure 3: The Langmuir isotherm for the adsorption of di (2-ethylhexyl) phthalate by cellulose nanofiber for the adsorbent dosage equal to 0.5 gr/L, contact time equal to 30 minutes, and pH = 7

Information related to value of the isolation factor have been mention in Table 5 and represented as a diagram in Figure 4.

Table 5: The value of the isolation parameter based on the Langmuir adsorption isotherm

Value of separation factor	Initial DEHP concentration (mg/l)
0.84	1
0.73	2
0.52	5
0.35	10

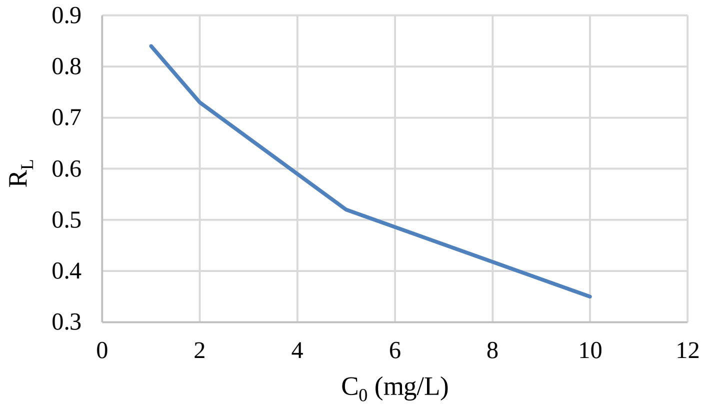

Figure 4: The value of the isolation factor for the adsorption of di (2-ethylhexyl) phthalate by cellulose nanofiber

Adsorption Kinetic

The obtained data was matched with the pseudo-first-order and pseudo-second-order models in order to analyze the mechanism of adsorption of di (2-ethylhexyl) phthalate. The values obtained for the two models have been provided in Figures 5 and 6 and Table 6. As can be observed, the pseudo-second-order model for the process is more valid and has the highest correlation coefficient.

Table 6: The coefficients and constants of the kinetic models

Pseudo second-order			Pseudo first-order		
R^2	q_e (mg/g)	K_2	R^2	q_e (mg/g)	K_1
0.9674	11.83	0.0205	0.4141	1.204	0.0058

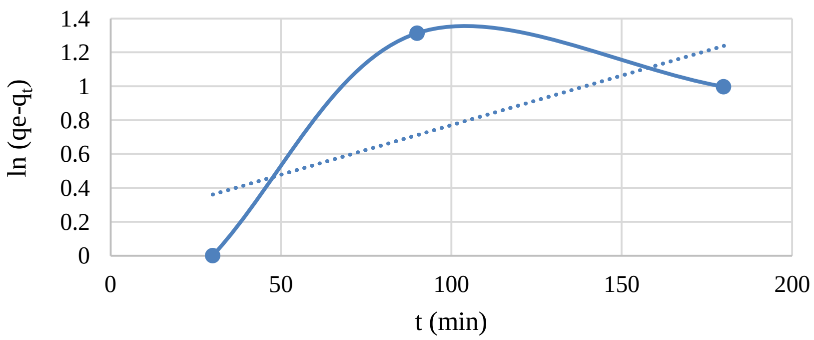

Figure 5: The pseudo-first-order kinetic for the adsorption of di (2-ethylhexyl) phthalate by cellulose nanofiber for a concentration of di (2-ethylhexyl) phthalate equal to 10 mg/L, adsorption dosage equal to 0.5 gr/L, and pH = 7.

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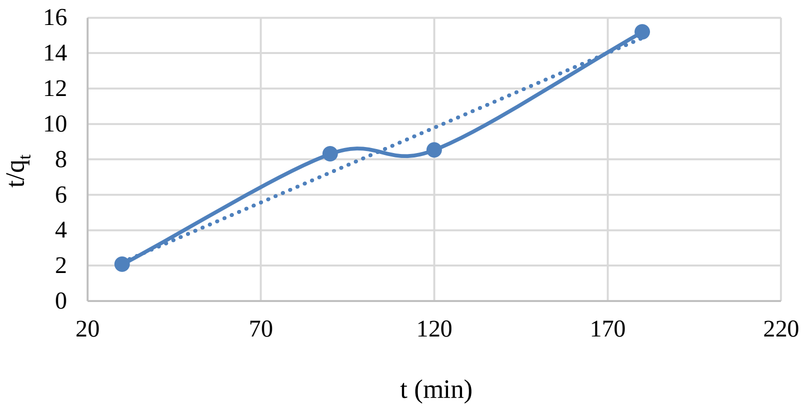

Figure 6: The pseudo-second-order kinetic for the adsorption of di (2-ethylhexyl) phthalate by cellulose nanofiber for a concentration of di (2-ethylhexyl) phthalate equal to 10 mg/L, adsorption dosage equal to 0.5 gr/L, and pH = 7.

Discussion

Adsorbent Isotherms Studies

One of the basic parameters in designing an adsorption system is the adsorption equilibrium isotherm, which describes the surface characteristics of the absorbents [26]. In fact, the adsorption isotherm indicates the relation between the amount absorbed per unit weight of the adsorbent and the amount of the adsorbate component remaining in the solution at equilibrium. As a result, the adsorption equilibrium models of Freundlich (multilayered adsorption) and Langmuir (monolayer adsorption) were used to determine the adsorption capacity of the cellulose nanofiber. In the Langmuir model, which is used to describe the homogeneous system, it is assumed that all the active sites are uniformly distributed across the whole surface of the adsorbent and have same or similar energies for the adsorption of the adsorbate component and in fact, there is no interaction between the adsorbate components. But in the Freundlich model, the available areas on the surface of the adsorbate object are independent and their powers are different for the adsorption of the adsorbate molecule due to various active sites [27, 28]. In this study, by comparing the values of R^2 obtained from the models, it is clear that the adsorption process of di (2-ethylhexyl) phthalate is more in accordance with the Langmuir model due to the higher correlation coefficient (0.95). This may be due to the uniform distribution of the adsorption sites on the adsorbent surface [28]. Mohan et al., in their evaluation of the removal of di (2-ethylhexyl) phthalate by activated carbon reported that the adsorption process follows both the Freundlich and Langmuir models [20]. according to the data from this study, the value of the maximum adsorption capacity (q_m) has also been obtained to be 312.5 mg/gr, which is more than the values reported for the adsorption of Acid Orange 7 through soy (17.544 mg/gr) [21], the adsorption of Janus Green B (21.6 mg/gr) and Methylene Blue (16.7 mg/L) through monocrystalline cellulose [19], the removal of nickel (119.05 mg/gr) and cadmium (132.48 mg/gr) through cherry branches, and the removal of nickel (134.05 mg/gr) and cadmium (246.87 mg/gr) through beech peel [28]. given that the value of di (2-ethylhexyl) phthalate is in a range between 1 and 10 mg/L, the value of the isolation factor was also found to be in a range between 0.35 and 0.84; it can thus be concluded that the adsorption system is favorable in this process.

Adsorption Kinetic Studies (Pseudo-First Order and Pseudo-Second Order)

Kinetic studies evaluate the effect of the contact time as an important factor along with the value of the adsorbate component in the adsorption process [29]. An important factor which is highly important in the design of an adsorption system is the prediction of the total adsorption velocity on the adsorbent surface. In fact, the study of the kinetic system is important due to the information it yields about the pollutant adsorption time as well as the volume of the reactor [30]. In other words, the kinetic studies provide some important information about the favorable conditions of the operation of discontinuous processes in real scale [31]. In chemical adsorption, it is assumed that the adsorption capacity is proportional to the number of occupied active sites on the surface of the adsorbent [32]. Pseudo-first-order and pseudo-second-order kinetic models are examples of absorption reaction models. The velocity of occupying adsorption sites in a pseudo-first-order model is proportional to the number of unoccupied sites on the adsorbent surface and in the pseudo-second-order models, this velocity is proportional to the square of the number of unoccupied sites [21]. The results obtained from this evaluation indicate that the adsorption of di (2-ethylhexyl) phthalate by cellulose nanofiber follows the pseudo-second-order model. The results are consistent with the results obtained by Samiyeh et al. for the removal of Janus Green B and Methylene Blue from aqueous solutions through monocrystalline cellulose [19] as well as with the study by Ferasati et al. on nitrate removal from aqueous solutions through modified Phragmites australis nanoparticles [33]. A comparison of the maximum adsorption (q_{max}) of cellulose nanofiber with other reported adsorbents for the removal of phthalate esters has also been provided in Table 7.

Table 7: Comparing the maximum adsorption (q_m) of phthalate esters by cellulose nanofiber with other adsorbents

Reference	Types of adsorbent	Types of phthalate esters	(mg/g) q_{max}
23	Polymer (GPP) γ-cyclodextrin polyurethane	DMP	13.64
23	Polymer (GPP) γ-cyclodextrin polyurethane	DEP	15.82
23	Copolymer γ -cyclodextrin/starch polyurethane (GSP)	DMP	15.10
23	γ -cyclodextrin/starch polyurethane copolymer (GSP)	DEP	17.38
23	Polymer starch polyurethane (SSP)	DMP	10.89
23	Polymer starch polyurethane (SSP)	DEP	12.13
34	Magnetic poly (EGDMA–VP) beads	DEP	119
35	Multiwalled carbon nanotubes	DEP	8.5
36	Activated carbon developed from phoenix leaves	DBP	133.33

Adsorption Mechanism of Di (2-Ethylhexyl) Phthalate through Cellulose Nano Fiber

The units forming cellulose have been linked to each other with beta bonds 1 to 4. The oxygen atoms of glycosidic bond and a pyranose ring together form a network of hydrogen bonds. Intermolecular hydrogen bonds between the cellulose nanofiber and carboxy di (2-ethylhexyl) phthalate are introduced as the adsorption mechanism of this pollutant through cellulose nanofiber.

Conclusion

This research indicates that the cellulose nanofiber is an effective adsorbent for the removal of di (2-ethylhexyl) phthalate from aqueous solutions. The adsorption process of di (2-ethylhexyl) phthalate follows the pseudo-second-order kinetic model. The adsorption isotherm studies indicated that the obtained results have more accordance with the Langmuir model. The value of the maximum adsorption was also calculated to be equal to 312.5 mg/gr, in keeping with the Langmuir model. It can be concluded that the cellulose nanofiber is an effective, efficient, and biodegradable adsorbent which can be used to reduce pollution of aqueous solutions.

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Conflict of interest

The authors have declared no conflict of interest.

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