



## Evaluating the efficiency of cellulose nanofibers in DEHP removal from water

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### ABSTRACT

The removal of di(2-ethylhexyl)phthalate (DEHP) from aqueous solutions by cellulose nanofibers (CNFs), derived from softwood, was studied. The optimum conditions of four factors at four levels including the DEHP concentration (1–10 mg/L), adsorbent dose (0.5–3 g/L), contact time (30–180 min), and pH (3–9) in a batch system was investigated by the design of experiment software. The Isotherm Fitting Tool software was used to fit isotherm parameters to experimental data. The maximum removal efficiency, (74.1%), was obtained at a DEHP concentration of 10 mg/L, an adsorbent dose of 0.5 g/L, a contact time of 30 min, and a pH of 7. The amount of DEHP adsorbed per unit weight of adsorbent ( $q_e$ ) in the optimum conditions was 14.8 mg/g. The system was well corresponded by the generalized Langmuir–Freundlich model. The results showed that extracted CNF from softwood has a good potential for treatment of polluted aqueous solutions by DEHP.

*Keywords:* Cellulose nanofiber; Adsorption; Di(2-ethylhexyl)phthalate; Aqueous solutions

### 1. Introduction

Phthalic acid esters are hazardous chemical materials that play an important role in the human health and environmental quality [1]. They are a category of flexible and pliable chemicals that are mainly used as plasticizers to increase the flexibility of plastic polymers such as polyvinyl chloride (PVC) [2]. Di(2-ethylhexyl)phthalate (DEHP), which contains alkyl chains with a backbone length of 3–6 carbons, is one of the commercially available phthalate esters and commonly used as plasticizer in PVC [3,4]. These compounds are used for producing paints,

varnishes, adhesives, personal care products, cosmetics, paper coating, pesticide, building products, and medical devices. So, it can be found in surface, ground, drinking, and bottled waters because of the discharge of untreated industrial wastewater and municipal sewage [2,5,6]. Potential pathways of exposure to phthalates are food, dermal contact, and inhalation in the general population [7]. During the production and processing, DEHP can be released into the environment through wastewater [5]. The United States Environmental Protection Agency (USEPA) has classified DEHP as a priority environmental pollutant, which is a probable human carcinogen. Hence, it is

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considered as a chemical of concern [1,2,8]. Because of some detriments, such as anti-androgenic, mutagenic, teratogenic, carcinogenic toxic, reproductive poisoner, and human endocrine disrupting system, DEHP is considered as an important concern among the scientific community and should be emitted from the environment [1,9,10]. According to the World Health Organization (WHO) Guideline value, the maximum allowable level of DEHP in drinking water is 0.008 mg/L [11]. There are some methods to reduce DEHP concentration in the aqueous environment: (1) aerobic and anaerobic biodegradation. It takes a long time because of the slow speed of hydrolysis and photolysis. Furthermore, microorganisms cannot completely remove DEHP from an aqueous solution. (2) Advanced oxidation processes using a combination of hydrogen peroxide ( $H_2O_2$ ), ozone ( $O_3$ ), sonolysis, photocatalysis, and ultraviolet radiation. High cost of operation is a challenge facing this method. (3) Physical and chemical processes such as coagulation/flocculation, floatation, and adsorption [6,12]. Among various methods, biosorption has extensively been reported because of some benefits such as its cost-effectiveness, simplicity, and high efficiency, along with the possibility of being regenerated and decreased chemical use and sludge production [13–15].

Cellulose is a natural linear polymer and the most abundant biorenewable, biocompatible, and environmentally friendly material on earth [16–18]. Cellulose nanofibers (CNFs) are one of the major structures of nanocellulose that are mainly extracted from lignocellulosic sources such as plants. CNFs diameters are usually below 100 nm. These materials are considered owing to their potential advantages such as low density, low cost, high surface area, high aspect ratio, and good mechanical properties [19,20]. CNFs could be delivered from some materials such as wood. In the past few years, numerous studies reported the removal of pollutants by different cellulosic sources from aqueous solutions. Hokkanen et al. [21] could effectively remove heavy metals from aqueous solutions by using succinic anhydride modified mercerized nanocellulose. Sureshkumar and Namasivayam [22] investigated the adsorption behaviour of Direct Red 12B and Rhodamine B from water onto the surfactant modified coconut coir pith and the method was found to be effective. Weng et al. [23] demonstrated that pineapple leaf powder (PLP) adsorbed methylene blue (MB) from aqueous solutions successfully. Namasivayam and Sureshkumar [24] indicated that the surfactant modified coconut coir pith is efficient as a biosorbent in chromium(VI) absorption from water and wastewater. In another study, Hafshejani et al. [25] found the nanostructured cedar leaf ash as a potent adsorbent for the removal of zinc and lead from aqueous solutions.

The aim of this study was to use CNFs extracted from softwood as an adsorbent for DEHP removal from aqueous solutions. To the best of our knowledge, no attempt has been made in this field. The effects of different variables, including an initial concentration of DEHP, adsorbent dose, contact time, and pH of solutions on adsorption efficiency, were investigated and the optimum conditions were determined.

## 2. Materials and methods

### 2.1. Materials

DEHP (chemical formula  $C_{24}H_{38}O_4$ , CAS number 117-81-7 ( $\geq 99.5\%$ )), HCl ( $\geq 37\%$ ), and NaOH ( $\geq 98\%$ ) (for pH

adjustment) were purchased from Sigma-Aldrich (USA). Carbon tetrachloride ( $\geq 99\%$ ; as extraction solvent) and acetonitrile ( $\geq 99.9\%$ ; as disperser solvent) were provided by Merck (Germany). CNFs gel ( $\geq 99\%$ ; with average diameter of 35 nm) was supplied by Nano Novin Polymer (Mazandaran, Iran). In order to remove the water phase, CNFs gel was centrifuged twice at 10,000 rpm for 10 min.

### 2.2. Experimental setup

The stock standard solutions of DEHP were prepared in deionized water at a concentration of 1,000 mg/L, and were placed in an ultrasonic bath for complete homogenization (Bandline Sonorex Digitex DT156, Sonorex Digitex Company, Germany) for 60 min. Then, they were stored at 4°C in a refrigerator.

Batch adsorption experiments were conducted using 110 mL glass bottles. An appropriate amount (0.5, 1, 2, and 3 g/L) of adsorbent was added to 100 mL of the DEHP solution at initial concentrations ( $C_0$ ) of 1, 2, 5, and 10 mg/L (derived from the stock standard solution) and the solution pH was adjusted to 3, 5, 7, and 9 using 0.1 M HCl and 0.1 M NaOH. The glass bottles were sealed with 20 mm stoppers. The headspace within each glass bottles was minimized to exclude any contaminant volatilization phenomena. The glass bottles of the batch experiments were stirred by a shaker (Orbital Shaker Model KS260B, IKA Company, Germany) at 250 rpm for 30–180 min at room temperature. Then, the solution samples were passed through the Whatman filter. Finally, the DEHP concentration in the liquid phase was determined using gas chromatography–mass spectrometry (GC/MS). Blank experiments, without the addition of adsorbents, were also conducted to ensure that the decrease in the DEHP concentration was not due to adsorption on the wall of the glass bottle or volatilization. The amount of the adsorbed DEHP on the adsorbent ( $q_e$ , mg/g) and the removal efficiency (%) of DEHP were determined from Eqs. (1) and (2), respectively:

$$q_e = (C_0 - C_t) \times \frac{V}{m} \quad (1)$$

$$\text{Removal (\%)} = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (2)$$

where  $C_0$  and  $C_t$  (mg/L) are DEHP concentrations at the beginning and after a certain period of time,  $V$  is the initial solution volume (L), and  $m$  is the adsorbent weight (g).

### 2.3. Extraction procedure and instrumentation

The extraction was carried out by dispersive liquid–liquid microextraction. 5 mL of the sample was placed in a screw cap glass test tube with conic bottom and then an appropriate amount of a mixture, including 750  $\mu$ L acetonitrile (as dispersive solvent) and 50  $\mu$ L carbon tetrachloride (as extraction solvent), were rapidly injected into the sample solution. At the end of this stage, a cloudy solution (sample, acetonitrile, and carbon tetrachloride) was formed in the test tube. The mixture was centrifuged at 4,500 rpm for 5 min and the fine droplets of extraction

solvent (carbon tetrachloride) were settled at the bottom of the conical test tube. 3  $\mu$ L of the settled phase was collected by using the microsyringe and injected into GC–MS system.

The analysis was carried out by the Agilent technology 7890A (USA) gas chromatograph coupled with a 5975C mass selective detector (MSD) system. A silica-fused HP5 column (30 m long  $\times$  0.25 mm internal diameter  $\times$  250  $\mu$ m film thickness) was used for separation and quantification. The major parameters were: injector temperature, 250°C; transfer line temperature, 290°C; ion source temperature, 230°C; carrier gas: He and flow rate, 1 mL/min; injection mode, split (10:1); and injection volume, 3  $\mu$ L. The programme of oven temperature was as follows: 100°C for 3 min, increasing temperature to 210°C at the 10°C/min heating rate, increasing temperature to 250°C at the 5°C/min heating rate, and increasing temperature to 280°C at the 30°C/min heating rate (held for 4 min). The total run time was 27 min. MSD ChemStation was applied for output data analysis.

Table 1  
Controlling factors and their levels

Factors	Level 1	Level 2	Level 3	Level 4
DEHP concentration (mg/L)	1	2	5	10
Adsorbent dose (g/L)	0.5	1	2	3
Contact time (min)	30	60	120	180
pH	3	5	7	9

Table 2  
Design matrix and results of DEHP removal by CNFs in different conditions

Run	Factors					Response 1: DEHP	
	DEHP concentration (mg/L)	CNFs dose (g/L)	Time (min)	pH	$C_i$	$R$ (%)	$q_e$ (mg/g)
1	1	2	60	5	0.8	20.5	0.1
2	5	3	30	5	2.3	54	0.9
3	10	0.5	30	7	2.6	74.1	14.8
4	10	3	60	9	3.5	64.5	2.2
5	2	0.5	120	5	1	50.1	2
6	10	1	180	5	3.6	64.2	6.4
7	1	0.5	180	9	0.9	12.4	0.3
8	1	1	30	3	0.6	36.4	0.4
9	2	2	30	9	1	50.2	0.5
10	5	2	180	7	2.4	52.9	1.3
11	2	1	60	7	1.5	24.6	0.5
12	2	3	180	3	1.2	40	0.3
13	10	2	120	3	3.8	61.8	4
14	5	0.5	60	3	2.3	54.2	5.4
15	5	1	120	9	2.2	56.2	2.8
16	1	3	120	7	0.8	24.3	0.1

#### 2.4. Analysis of data

To determine optimum conditions in DEHP removal by the CNF, the design of experiment software (Design Expert 6 Stat-Ease, Inc., USA) was used. In this study, four factors at four levels were involved in the adsorption processes (Taguchi orthogonal array plan). These factors and levels are shown in Table 1. All experiments were repeated two times, and the mean values were reported. The adsorption isotherm of DEHP by CNFs in the optimum conditions with initial concentrations of DEHP (0–100 mg/L) was determined by the Isotherm Fitting Tool (ISOFIT) software. ISOFIT estimated 1 mg/L of water solubility ( $S_w$ ) for DEHP. The ISOFIT analysis fits the parameters of experimental data via the minimization of a weighted sum of squared error (WSSE) objective function. The ISOFIT supports several isotherms including (1) Langmuir, (2) Linear, (3) Freundlich with linear partitioning (F-P), (4) Langmuir with linear partitioning (L-P), (5) Freundlich, (6) Toth, and (7) generalized Langmuir–Freundlich (GLF).

### 3. Results

#### 3.1. Batch experiments performance

The DEHP removal efficiency by CNFs and its adsorption capacity ( $q_e$ ) on CNFs under different initial concentrations of DEHP, adsorbent CNFs doses, contact time, and pH values are shown in Table 2. The plots of the abovementioned parameters on the DEHP removal process by CNFs

are shown in Figs. 1–4 and the effect of the factors and their interactions are presented in Table 3.

### 3.2. Isotherm study

An isotherm study was performed for DEHP adsorption by CNFs in the batch condition. Table 4 shows the  $q_e$  for the

optimum conditions with different initial concentration of DEHP (0–100 mg/L), an adsorbent dose of 0.5 g/L, a contact time of 30 min, and pH 7. Table 5 summarizes some of the diagnostic statistics computed by ISOFIT and reported in the output file. In Table 6, Linssen measurement indicated significant WSSE non-linearity near the optimal parameter

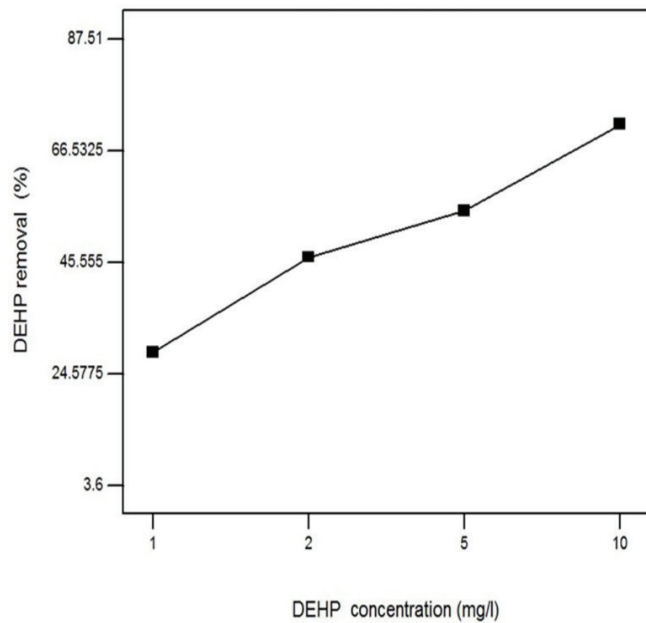


Fig. 1. Effect of initial DEHP concentration on its removal by CNFs: initial DEHP concentration (1–10 mg/L), adsorbent dose (0.5 g/L), contact time (30 min), and pH (3).

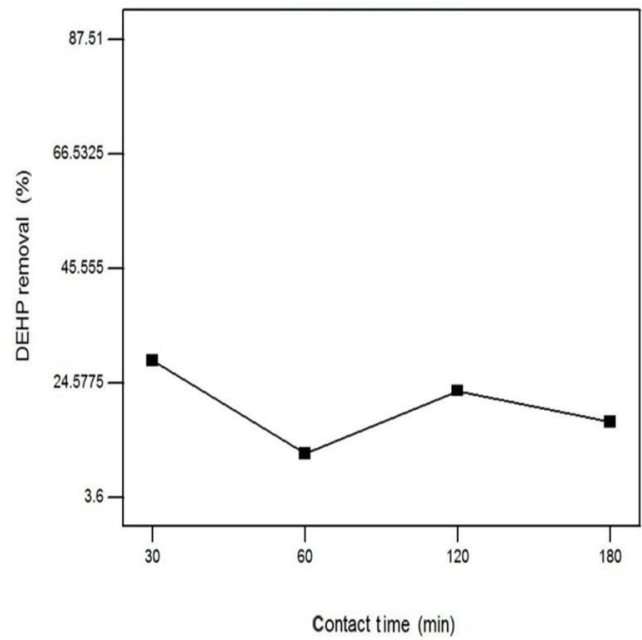


Fig. 3. Effect of contact time on DEHP removal by CNFs: contact time (30–180 min), initial DEHP concentration (1 mg/L), adsorbent dose (0.5 g/L), and pH (3).

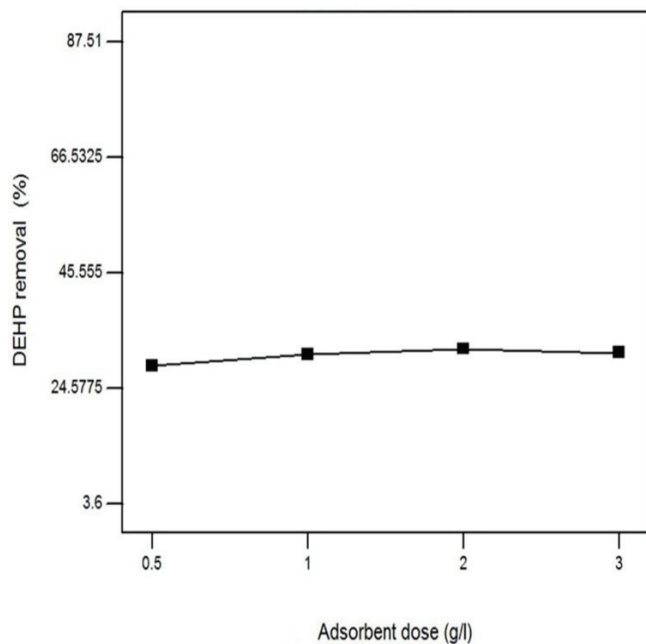


Fig. 2. Effect of adsorbent dose on DEHP removal by CNFs: adsorbent dose (0.5–3 g/L), initial DEHP concentration (1 mg/L), contact time (30 min), and pH (3).

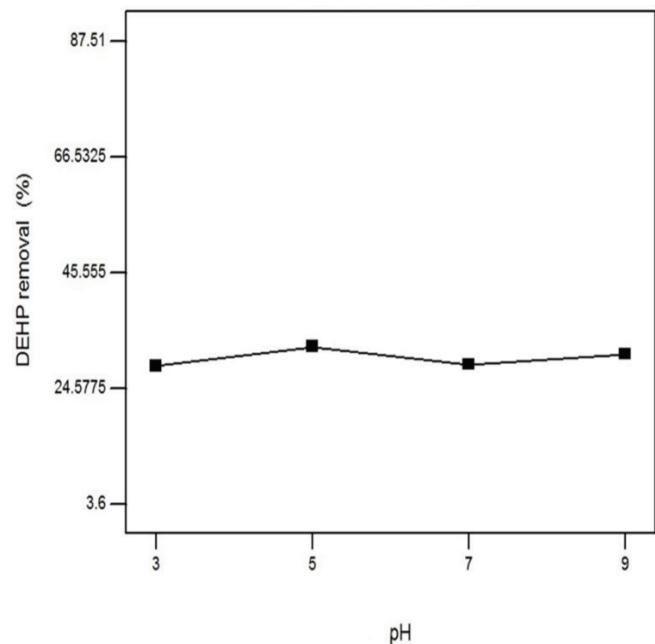


Fig. 4. Effect of pH on DEHP removal by CNFs: pH (3–9), initial DEHP concentration (1 mg/L), adsorbent dose (0.5 g/L), and contact time (30 min).

Table 3  
Effects of the factors and interactions for DEHP removal by CNFs

Factor/interaction	Degrees of freedom	Sum of squares	Mean squares	F value	P value	Contribution (%)
A: DEHP concentration (mg/L)	3	7,630.7	2,543.6	9.4	0.0008	54.1
B: Adsorbent dose (g/L)	3	40.7	13.6	0.1	1	0.3
C: Contact time (min)	3	1,299.2	433.1	1.6	0.2	9.2
D: pH	3	65	21.7	0.1	1	0.5
AB interaction	3	722.3	240.8	0.9	0.5	5.1

Table 4  
Adsorption capacity of DEHP by CNFs in different DEHP initial concentration

Initial DEHP concentration (mg/L)	Adsorption capacity ( $q_e$ ) (mg/g)
0	0
10	14.5
20	32.8
30	52.9
40	73.3
50	89
60	111
70	132.1
80	149.3
90	168.3
100	184.2

values. Statistical measures such as  $R_N^2$  and Durbin–Watson test ( $D$ ) imply normally distributed weighted residuals with no serial autocorrelation. Fig. 5 contains the plot of the fitted isotherm that is organized into visually indistinguishable groups along the observed data points.

#### 4. Discussion

According to Table 2, the maximum adsorption of DEHP, >74%, was observed during run 3.

##### 4.1. Effect of initial concentration on DEHP removal

The results demonstrated that the initial concentration of DEHP has a significant influence on its removal. From Fig. 1, as the initial concentration of DEHP rises from 1 to 10 mg/L, the DEHP adsorption increases from 28.58% to 71.36%. Increasing the initial concentration of DEHP enhanced the adsorption capacity, mainly due to the increased collision frequency per unit time between CNF and DEHP as well as the fraction of collisions occurring with the correct orientation [26]. These results were consistent with several already quoted reports of phthalates absorption by other adsorbents. The mechanism of dialkyl phthalates removal from aqueous solutions using  $\gamma$ -cyclodextrin and starch-based polyurethane polymer adsorbents

was investigated by Okoli et al. [27]. They concluded that by increasing the phthalate aqueous concentration, its adsorption from aqueous solutions increased. Özer et al. [28] declared that the amount of diethyl phthalate (DEP) adsorbed by magnetic poly(EGDMA–VP) beads increased along with an increase in the initial concentration of DEP from 1 to 500 mg/L, but this increase reached the equilibrium at a DEP concentration of 500 mg/L. A similar trend was previously reported by Weng et al. [23]; they found that with an increase in the initial concentration of MB, its adsorption onto the PLP increased. But contradictory results have been reported by Salam et al. [29] in terms of the removal characteristics of heavy metals from wastewater by low-cost adsorbents.

##### 4.2. Effect of adsorbent doses on DEHP removal

Fig. 2 shows that variations in the amount of extracted nanofiber from softwood do not have any significant influence on DEHP adsorption from aqueous solutions. Based on Fig. 2, the adsorbent dose of 0.5 g/L was selected as the optimum dose in DEHP removal by CNFs. This observation can be attributed to the tendency of CNFs to aggregate. A probable mechanism is that there is a competition for DEHP–CNF and CNF–CNF hydrogen binding. At relatively high concentrations of CNF, an interfiber hydrogen bonding area is formed and cellulose chains are easily self-assembled, so the accessibility of surface hydroxyl groups decreases and consequently the absorption yield is not changed, significantly, by increasing CNF loading. For some time, contradictory results have been reported in the literature. For example, Okoli et al. [27] showed that with an increase in  $\gamma$ -cyclodextrin and starch-based polyurethane polymer doses as adsorbents (from 10 to 100 mg), the percentage of DEP removal from aqueous solutions increased. Hafshejani et al. [25] reported that increasing the nanostructured cedar leaf ash dose within the studied range (10–20 g/L) increased the adsorption efficiency of  $Pb^{2+}$  and  $Zn^{2+}$  ions from aqueous solutions, but the adsorption efficiency decreased at higher adsorbent dosage (20–50 g/L) because of the aggregation of active sites. In addition, Mohan et al. [30] presented a direct relation between the dosage of activated carbon and DEP adsorption from aqueous phases. Similar effects were reported by Sureshkumar and Namasivayam [22] for dyes removal using the surfactant-modified coconut coir pith.

##### 4.3. Effect of contact time on DEHP removal

According to Fig. 3, the maximum DEHP removal occurred after 30 min of the exposure. So, the 30 min contact

Table 5  
Summary of selected diagnostics for DEHP adsorbed by CNFs

Isotherms	AICc <sup>a</sup>	$R_f^2$ <sup>b</sup>	$R_N^2$ <sup>c</sup>	$M^{2d}$	Linearity assessment
GLF	13.6	1	0.942	$1.12 \times 10^3$	Non-linear
Linear	21.3	0.999	0.949	$5.99 \times 10^{-9}$	Linear
Langmuir	21.3	0.999	0.949	$5.93 \times 10^{-9}$	Linear
L-P	24.5	0.999	0.949	2.4	Non-linear
Freundlich	24.5	0.999	0.949	19.4	Non-linear
F-P	29.7	0.999	0.954	14.6	Non-linear
Toth	71	0.977	0.915	3.9	Non-linear

<sup>a</sup>AICc = multi-model ranking.

<sup>b</sup> $R_f^2$  = correlation between measured and simulated observation.

<sup>c</sup> $R_N^2$  = correlation between residual and normality.

<sup>d</sup> $M^2$  = Linssen measure of non-linearity.

Table 6  
Selected ISOFIT post-regression output (GLF isotherm)

Parameter or statistic	ISOFIT result	
Overall quality of fit	WSSE	14.3
	RMSE	1.3
	$R_y$	1
Parameter statistics	$bQ_0$	2.87
	$b$	$3.12 \times 10^{-3}$
Parameter standard error	$bQ_0$	$3.26 \times 10^{-1}$
	$b$	$1.15 \times 10^{-3}$
Test of assumptions Linssen ( $M^2$ )	$M^2$	$1.12 \times 10^3$
	Threshold	$2.30 \times 10^{-1}$
Normality ( $R_N^2$ )	Assessment	Non-linear
	$R_N^2$	0.942
	Critical value	0.71
Runs test	Assessment	Normal residuals
	Number of runs	5
	$P$ value	0.36
Durbin–Watson test ( $D$ )	Assessment	No correlation
	$D$	2.37
	$P$ value	0.64
	Assessment	No correlation

time was selected as the optimum time for DEHP adsorption by CNFs. No significant change in the removal efficiency occurred after 30 min. It can be concluded that most of reaction sites of the CNF are exposed for interaction with DEHP during the initial exposure period and hence the uptake rate of pollutant is quite rapid. These results are in agreement with the observed insignificant effect of time on the amount of adsorbed metal ions ( $\text{Cu}^{2+}$ ) from aqueous solutions onto the iron oxide coated eggshell powder after 180 min [31].

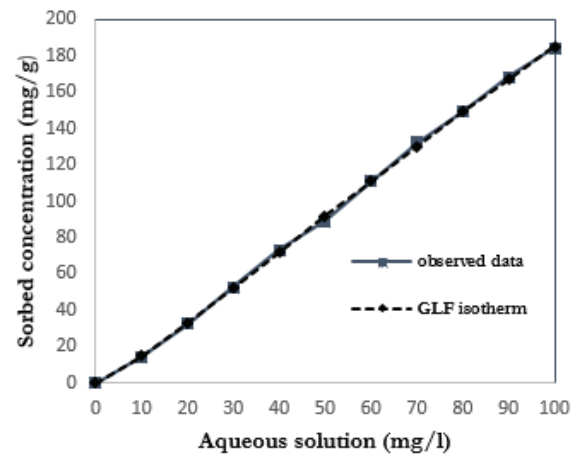


Fig. 5. Plot of fitted isotherm and observed data: GLF.

#### 4.4. Effect of pH on DEHP removal

Fig. 4 and Table 3 demonstrate the effect of pH on the removal percentage of DEHP by CNFs. As can be seen, the pH solution does not significantly affect the removal percentage of DEHP. Therefore, pH 7 was considered as the optimum pH for DEHP adsorption by CNFs. The pH of the media significantly influence the uptake of materials as it determines the degree of ionization, speciation of the adsorbate, and the surface charge of the adsorbent. Considering the presence of two alkyl chains, along with a benzene ring without any ionizable group in the chemical structure of DEHP, no significant impact of pH on its removal yield is expected. Corroborating results have been reported in the removal of phthalate esters by the  $\alpha$ -cyclodextrin-linked chitosan bead [32], adsorption of phthalate ester on molybdate impregnated chitosan beads [33], and coextractive extraction of phthalates from water where pH changes did not affect the adsorption efficiency [34]. Salam et al. [29] apperceived  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ion removal by different adsorbents such as natural zeolite, peanut husk, and fly ash within the pH range of 4–7 efficaciously. Wang [35] observed that at various pH values (1–7), the dibutyl phthalate adsorption capacities onto

activated carbon, developed from phoenix leaves, kept stable but when the initial pH value changed from 9 to 13, adsorption capacities increased. Shukla et al. [36] stated that most of the metal adsorption on sawdust has been increased by increasing pH within a distinctive pH range, followed by a decrease with additional pH increase.

In addition, as shown in Table 3, there was an interaction between the initial concentration of DEHP and the CNFs dose.

There is a significant statistical difference between the mean square of parameters against the experimental error. Here, the DEHP concentration has a  $P$  value  $<0.05$  and showed that it is significantly different from zero at the 95% confidence level. The  $F$  value test indicated that the DEHP concentration affected the adsorption performance significantly. Considering the  $F$  values of 1.6, 0.1, and 0.9 for the contact time, pH, and interaction between DEHP concentrations and adsorbent dose, their influences on the adsorption efficiency were less significant compared with DEHP concentration.

The effectiveness of the abovementioned factors on the removal of DEHP are as the following: DEHP concentration  $>$  contact time  $>$  DEHP concentration and CNFs dose interaction  $>$  pH  $>$  adsorbent dose. Thus, the removal of DEHP by CNFs was calculated by Eq. (3):

$$\begin{aligned} \text{Removal of DEHP (\%)} = & 45.19 - (20.97 \times \text{DEHP concentration} \\ & (\text{mg/L})) - (0.49 \times \text{CNFs dose (g/L)}) \\ & + (2.8 \times \text{contact time (min)}) \\ & - (0.64 \times \text{pH}) \end{aligned} \quad (3)$$

Table 5 shows the corrected akaike information criterion (AICc) values, indicating that the GLF isotherm expression provides the best fit of the sorption data based on its relatively lowest value of multi-model ranking. The GLF constant  $b$  was calculated to be less than unity for most of the adsorbate and adsorbent combinations, indicating that the adsorption of the selected contaminants onto the CNFs samples is favourable. Non-linear regression techniques overcome many of the deficiencies associated with trial-and-error and linearization approaches for isotherm fitting. However, the performance of non-linear regression techniques can be impeded by the presence of local minima or excessive parameter correlation. Table 6 contains selected ISOFIT output for the GLF isotherm. ISOFIT provides two 'standard' measures for evaluating the isotherm goodness of fit, namely the root mean squared error (RMSE, Eq. (4)) and the correlation between measured and fitted observations ( $R_y$ , Eq. (5)):

$$\text{RMSE} = \sqrt{\frac{\text{WSSE}}{(m-p)}} \quad (4)$$

$$R_y = \frac{\sum_{i=1}^m (w_i S_{i,\text{obs}} - S_{\text{obs}}^{\text{avg}})(w_i S_i - S^{\text{avg}})}{\sqrt{\sum_{i=1}^m (w_i S_{i,\text{obs}} - S_{\text{obs}}^{\text{avg}})^2 \sum_{i=1}^m (w_i S_i - S^{\text{avg}})^2}} \quad (5)$$

where WSSE is the weighted sum of squared errors,  $m$  is the total number of experimental observations,  $p$  is the number of isotherm parameters,  $w_i$  is the weight given to observation

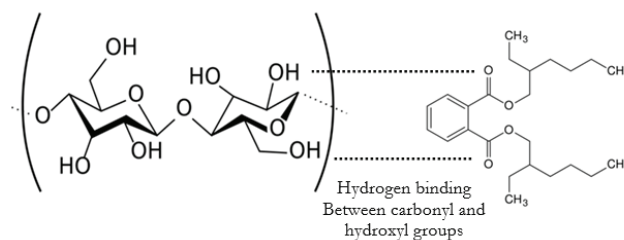


Fig. 6. Mechanism of DEHP adsorption on CNFs.

$i$ ,  $S_{i,\text{obs}}$  is the  $i$ -th experimentally measured sorbed concentration,  $S_i$  is the  $i$ -th simulated sorbed concentration computed via an isotherm expression, and  $S_{\text{obs}}^{\text{avg}}$  and  $S^{\text{avg}}$  are the averages of the weighted measured and weighted isotherm-simulated adsorbed concentrations, respectively.

#### 4.5. Adsorption mechanism

Cellulose is a high molecular weight homopolymer of  $\beta$ -1,4-linked anhydro-d-glucose units. Because of the glucose structure, cellulose has plenty of hydroxyl groups. The OH groups on  $C_1$  and  $C_4$  of monomeric units are involved in  $\beta(1 \rightarrow 4)$  glycosidic bonds. Oxygen atoms of the glycosidic linkage and the pyranose ring, together with the free OH groups located at the  $C_2$ ,  $C_3$ , and  $C_6$  form an extensive intramolecular and intermolecular hydrogen bond network. While the intramolecular hydrogen bonds are responsible for the rigidity and linear integrity of the cellulose chain [37], intermolecular hydrogen bonds between CNF and carbonyl moieties of DEHP and London–van der Waals forces (physical absorption) can be introduced as a proposed mechanism for the removal of this pollutant by this absorbent. In addition, the high surface area offers large numbers of accessible OH groups on the CNF surface, thus making it a suitable candidate for adsorptive removal in wastewater treatment [38]. The suggested mechanism of DEHP adsorption on CNFs is presented in Fig. 6.

## 5. Conclusion

CNFs derived from softwood were selected for studying the biosorption of DEHP from aqueous solutions. High removal was recorded at a DEHP concentration of 10 mg/L, an adsorbent dose of 0.5 g/L, a contact time of 30 min, and pH 7. The obtained results showed that initial DEHP concentrations affected the biosorption process significantly, but the adsorbent dose, contact time, and pH values did not significantly influence the DEHP removal efficiency. The GLF isotherm model described the equilibrium adsorption data better than other alternative isotherms within the examined concentration range. This biosorbent can be used as an efficient adsorbent to remove DEHP from wastewater and polluted water.

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