Continuous Fixed-Bed Column Study Using Carbon Nano-Adsorbent Made Through Pyrolysis of Garbage Leachate on the Sand Particles for Removal of 4-Nonylphenol from Surface Water

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Abstract

The potential of carbon nanorods (NRs) derived from garbage leachate was assessed in a fixed-bed and batch system replacing the present costly approaches to treat surface water polluted by 4-Nonylphenol. First, the waste leachate was coated on silica particles and then pyrolysis was performed at 300 to 800°C. The optimum temperature for the production of nano-adsorbent was determined by analyses such as scanning electron microscopy (SEM) for adsorbent morphological characterization, X-ray energy dispersive spectrometry (EDS), and Raman test. Next, Freundlich, Langmuir, and UT isotherm models were used to analyze the batch equilibrium data. The impact of inlet 4-NP concentration (0.5, 1, and 2 mgL⁻¹), feed flow rate (5, 10, and 20 mLmin⁻¹), bed height (5, 10, and 15 cm), and bottom-up flow on the breakthrough features of the sorption system with a fixed bed was examined. The adsorption data were fitted using the well-known column models (i.e., Thomas, Yoon-Nelson, and Adams-Bohart). For all circumstances, the best fitting was obtained for the attained results using Yoon-Nelson and Thomas models, but not the Adams-Bohart model. The experimental data confirmed that increasing the inlet concentration and bed depth resulted in an increase in the adsorption capacity and a decrease in flow rate. After applying a different regeneration process, the results showed the effectiveness of the novel engineered substance as a reusable adsorbent for water treatment.

Keywords: Fixed-bed; 4-Nonylphenol; Removal; Garbage leachate; Sand particles; Carbon nano-adsorbent

1. Introduction

Water is a vital resource for human beings' life and its quality plays a key role in human health (Guimarães et al., 2018; Zhang et al., 2019; Zhao et al., 2020). Today, water resource has posed a rising concern in the view of socio-economic development (Araujo, Bauerfeldt, & Cid, 2017). Climate change projections have indicated that changing climate affects each component of the climate system with regional differences (Mosadegh, 2013; Mosadegh & Nolin, 2020; IPCC, 2021; Mosadegh et al., 2021). Projected climate change shows changes in patterns of climate variables such as temperature and precipitation which will consequently affect water resources (Mosadegh et al., 2013; Mosadegh & Babaeian, 2021, Mosadegh & Babaeian, 2021). The primary use of this resource or the public supply is compromised by a lack of sufficient basic sanitation (Atlantic & Dias, 2008; Vianna, 2015). Recently, the existence of some pollutants has attracted the attention of environmental experts particularly in aquatic settings (Regadio et al., 2012; Mosadegh et al., 2018; Mejia et al., 2019). The chemicals including pharmaceuticals and personal care products (PPCPs), endocrine-disrupting chemicals (EDCs), and persistent organic pollutants (POPs) are extensively utilized in different industries (Xia, Keller, & Wagner, 2001). The sludge and effluent of industrial and municipal wastewater treatment plants are the entry routes of emerging pollutants to water resources (Geissen et al., 2015). The search for more sources and further expensive and complex chemical treatments for ensuring accessibility of drinking water are other challenges in this regard (Araujo et al., 2017). Current studies have indicated that 4-NP is a robust estrogenic isomer probably entering the aquatic environment via the treated sewage effluent discharge. Therefore, NP is regularly discovered in the ultimate sewage treatment plant effluents owing to the persistence against complete biodegradation and lack of innovative wastewater (Bouki, C.; Dvorakova & Dvorakova, 2010).

Adsorption has been a key option as a result of the exclusive physicochemical features of NP like a high $\log K_{oc}$ value and low water solubility (Derco, Dudáš, Valičková, Sumegová, & Murínová, 2017; Ejraei, Ali, & Ziarati, 2019). The presence of NP was reported by Johnson et al. (Shin, Kim, & Park, 2019) in Europe for the effluent of 17 municipal WWTPs with concentrations within the range of 0.05-1.31 mg/L. Utilizing radiolabeled NP, Cirja et al. (Ejraei et al., 2019) indicated that complete volatilization and mineralization of NP had a role in removing less than 1% of NP from wastewater treated in a membrane bioreactor. The combined impact of bio-oxidation and sludge adsorption is the key removal mechanism for intermediate products. Nonetheless, some reports have indicated the low adsorption capacities of these materials and difficulties or efficiencies in their removal or regeneration (Abbas et al., 2016; Asmaly et al., 2015). Accordingly, it has been attempted to develop a novel adsorbent substance with easy regeneration and greater adsorption capacity for wastewater effective treatment. In this regard, there are some studies on CNTs and their composites, as well as the impact of operating parameters (Ahmad et al., 2017; Rajabi, Mahanpoor, & Moradi, 2017; Shouman & Fathy, 2018). Searching for a cost-effective and novel substance for water treatment is a persistent challenge worldwide. Carbon-based nanostructured materials (CNMs) are among the most versatile and robust contestants for effective water treatment (Selvaraj, Hai, Banat, & Abu, 2020). Today, other carbon structures are produced by the developments in novel technology like nano-adsorbents (Jin, Wang, Sun, Ai, & Wang, 2015). Despite the decent potential of nano-adsorbents in removing MP, they have somewhat problematic applications in the slurry state due to their essential removal in the ultimate treatment. The problems at the slurry state are solved by coating silica sand particles with nano-adsorbent. In this regard, the beneficial properties of silica grains have been enhanced for example in the creation of novel adsorbent NRs. This knowledge is an effective stage in silica grain improvement, although it has still a long way to practical use (Jin et al., 2015). Nanomaterials are extensively utilized as an adsorbent for removing pollutants from water/wastewater as a result of their exclusive features of high surface area to volume ratio. Thus, they are an appropriate candidate for developing future technology in water/wastewater treatment (Jawed, Saxena, & Pandey, 2020). The composition of garbage leachate is affected by numerous factors such as the type of deposited waste, the technique to exploit the landfill, the availability of oxygen, and the hydrogeological circumstances, and the landfill age (Yang et al., 2016). This issue has increased environmental and health risks (Toro-Vélez et al., 2016).

In the present study, the behavior of carbon nanorods (NRs) made by garbage leachate is investigated for adsorption of 4-NP bearing surface water in batch and fixed-bed sorption systems. This adsorbent was synthesized and coated on the sand particles at the same time. The garbage leachate was dried on the surface of the acid-washed sand particles and then pyrolyzed at different temperatures. In the next step, the optimum temperature for nano-adsorbent fabrication was selected, and experiments were performed to remove 4-NP at different concentrations with different doses of the adsorbent. Column dynamics were assessed using Yoon-Nelson, Thomas, and Adams-Bohart models. Recycling and column regeneration were performed until 7 cycles taking into account the prepared sorbent's industrial applicability.

2. Methods

2.1. Preparing nano-adsorbent

To prepare the nano-sorbent, 500 g sand was acid-washed with 500 mL of diluted hydrochloric acid (1:1) and heated for 3 hours. Next, it was rinsed with distilled water several times. The acid-washed sand particles were poured into the beaker containing 500 mL of the leachate. Then they were heated so that the leachate evaporated and the sand particles were covered with the leachate constituents. Afterward, they were dried in an oven at 100°C for 2 h. In the next step, they were placed in a furnace reaching 700°C for 40 min and keeping at 700°C for 1 h. The particles were rinsed with distilled water several times after cooling. Since the temperature can be an effective factor in the formation of carbon nanorods, the pyrolysis was performed at different temperatures ranging from 300 to 800°C.

2.2. Characterization

Scanning electron microscopy (SEM), Raman spectroscopy, and X-ray energy dispersive spectroscopy (EDS) were performed to characterize the chemical and physical features of the produced nano-adsorbent.

2.3. Reagents

The solvents, reagents, and other chemicals utilized in this work were bought from Merck, Germany. The concentration of the materials applied in the tests was obtained using the stock solution.

2.4. Determination of 4-NP

To determine the residual concentration of 4-NP, an HPLC (Agilent 1100) equipped with a C18 column (4.6 × 250 mm, 5 µm) and a UV detector was used in an isocratic elution with the constant composition of the mobile phase. The mobile phase included an acetonitrile-water mixture (80:20) with a flow rate of 1 mL/min. The samples were filtered before injection into the column using PTEF syringe filters (0.2 µm).

2.5. Batch adsorption investigation

The batch tests were performed by the addition of 0.1g of NRs in 100 mL of 4-NP solution (0.5, 1, and 2 mgL⁻¹) and shaking at 120 rpm until reaching equilibrium. The concentration of the remaining cations was studied followed by a set of time intervals until reaching equilibrium via an atomic absorption spectrophotometer (PerkinElmer Model 3100). At the equilibrium state, the quantity of adsorbed 4-NP, q_e (mg/g), was determined through Eq. (1):

$$q_e = \frac{(C_0 - C_e)}{W} \quad (1)$$

Where q_e (mgg⁻¹) is the quantity of 4-NP adsorbed at equilibrium. C_e and C_0 (mgL⁻¹) represent the liquid-phase concentrations of 4-NP at equilibrium and initial circumstances, respectively. $V(L)$ shows the solution volume and $W(g)$ represents the mass of applied NRs. To determine the removal efficacy of the 4-NP, the residual 4-NP concentration was divided followed by equilibrium through primary 4-NP concentration, and the outcome is determined on a percentage basis.

2.6. Column data analysis

Dynamic column investigations were performed within a glass column with the height and internal diameter of 30 cm and 2.54 cm, respectively. The preferred flow rate was maintained using a peristaltic pump. To avoid any loss of adsorbent and give mechanical support to the adsorbent bed, a ball of 0.05-cm thick glass wool was set on the bottom side. The entire test were performed at room temperature (26 ± 2°C). The procedure parameters' effects including flow rate (5, 10, and 20 mLmin⁻¹), bed depth (5, 10, and 15 cm), and concentration (0.5, 1, and 2 mgL⁻¹) were assessed. The specimens were gathered every 5 min from the bottom of the column and were examined for the 4-NP concentration. The column behavior was studied by determining the adsorption capacity and breakthrough time. The adsorption capacity at the breakthrough of 10% was determined as (Biswas & Mishra, 2015):

$$q_B = \left(\frac{x}{m} \right)_B = \frac{x_B}{m_{adsorbent}} = Q_v \left(C_0 - \frac{C_B}{2} \right) \frac{t_B}{m_{adsorbent}} \quad (2)$$

Where C_0 is the influent concentration (mgL⁻¹), x_B shows the mass of adsorbed in the column at breakthrough (mg), $m_{adsorbent}$ represents the mass of the adsorbent in the column (g), Q_v is the flow rate (mLmin⁻¹), C_B is the breakthrough concentration (mgL⁻¹), and t_B shows the time to breakthrough (min).

3. Results

3.1. The adsorbent features

SEM tests were performed for morphological detection of possible changes in sand-covered with waste garbage leachate and sand coated with carbon nanoparticles. According to the SEM images (Fig. 1c and 1h), no specific changes were observed in the raw and acid-washed sand particles, but in the sand coated with carbon nanoparticles, short nanorods, and a considerable alteration in the structural integrity of the adsorbent was observed. As can be seen in Fig.1, the nanoparticles, which were planar, formed at 400°C. However, they tend to be rod-shaped with increasing pyrolysis temperature.

Fig.1. (a) Sand particles covered with waste garbage leachate and **(b)** silica-coated with Nanoparticles (NRs); SEM images of nano-adsorbent at **(c)** 300°C, **(d)** 400°C, **(e)** 500°C, **(f)** 600°C, **(g)** 700°C, and **(h)** 800°C

Raman spectroscopy was applied to study chemical and intramolecular bonds (Goldstein & All, 2003). EDS is an analytical method for the chemical characterization or elemental analysis of a specimen. This technique works based on the interaction of a sample and some X-ray excitation sources. This method relies on the fundamental principle where each element possesses an exclusive atomic structure, permitting an exclusive set of peaks on its electromagnetic emission spectrum (Asmaly et al., 2015).

Fig. 2a shows the results of the Raman test. As can be seen, sand particles were covered with garbage leachate, leading to different peaks that may be due to different elements existing in the garbage leachate and their coverage at the sand surface. Moreover, the peaks showed the formation of NRs on the sand particles' surface. **Fig. 2b** illustrates the EDS results of the adsorbents produced in this study. As can be noticed, due to the leaching of sand on the sand, several elements deposit on the sand surface.

Fig.2. Silica-coated with NRs: (a) Raman test, **(b)** EDS test

3.2. Batch adsorption study

Freundlich and Langmuir's isotherms are the models commonly applied for modeling heterogeneous and homogenous surfaces, respectively. According to the Langmuir model, the adsorption capacity is correlated with the initial concentration of the adsorbent. Furthermore, the exponential distribution and energies of the active sites and the expression related to surface heterogeneity are represented through the Freundlich isotherm (Ayawei, Ebelegi, & Wankasi, 2017).

To examine batch equilibrium data, the linear form of the Langmuir isotherm equation was used as:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (1)$$

Where $q_{\max}$ (mgg^{-1}) shows the maximum quantity of the 4-NP per unit weight of the NRs to create a complete monolayer over the surface. Also, K_L (Lmg^{-1}) represents the Langmuir constant associated with the affinity of binding sites.

$$R_L = \frac{1}{1 + K_L C_0} \quad (5)$$

The essential features of the Langmuir equation are described based on a separation factor. Here, R_L is obtained as follows.

The linear form Freundlich isotherm is:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (6)$$

Where K (mgg^{-1}) denotes the multilayer adsorption capacity or affinity factor, and $1/n$ represents the adsorption intensity, respectively.

UT isotherm model (Amini et al., 2008) is a dose-dependent model capable of estimating the highest adsorption capacity of adsorbent with the heterogeneous surface. There is a relation between the adsorption capacity obtained utilizing the UT model and multi-layer adsorption. Here, the adsorption capacity attained from the Langmuir model is related to the monolayer adsorption over the adsorbent's surface. **Table 1** represents the errors and parameters of the three isotherm models for 4-NP adsorption. Based on the R^2 and error values, the Langmuir and Redlich-Peterson models were the most proper model to explain the 4-NP adsorption procedure. As previously mentioned, R_L denotes adsorption nature. For 4-NP, the quantity of R_L was within the range of 0.72-0.98 ($0 < R_L < 1$), indicating satisfactory adsorption.

Table 1. The isotherm parameters were obtained utilizing error values and linear regression for adsorbing 4-NP on the adsorbent

Isotherm	Equation	R^2	RMSE	χ^2	Parameter	Value
Freundlich	$\ln q_e = \ln K_F + \frac{1}{n_F} \ln C_e$	0.9995	0.0183	0.0020	n_F	1.055
					$K_F: \text{mgg}^{-1} (\text{L.mg})^{1/n}$	1.057
Langmuir	$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}$	0.9999	5.22×10^{-5}	2.11×10^{-8}	$q_m: \text{mgL}^{-1}$	6.447
					$K_L: \text{L mg}^{-1}$	0.1887
					R_L	0.72-0.98
UT Isotherm	$\ln(\frac{C_e}{C_e - K_d}) = -b \ln C_m + b \ln C_e$	0.9808	0.0046	0.0001	$q_m: \text{mg g}^{-1}$	1.4523
					$K_d: \text{mg L}$	0.0085
					b	0.1012
					FCF	0.0059

3.3. Column data analysis

3.3.1. The impact of 4-NP inlet concentration

The impact of 4-NP concentration on the column behavior was investigated by altering the inlet concentration (0.5, 1, and 2 mgL⁻¹) when using the feed flow rate of 20 mLmin⁻¹ and the same adsorbent bed height of 5 cm. **Fig. 3** represents the breakthrough curve where the NRs beds were fatigued sooner at a higher 4-NP inlet concentration of 2 mgL⁻¹. Hence, the former breakthrough point was obtained at higher concentrations. It was found that the breakpoint time was reduced by increasing 4-NP inlet concentration because of saturating the binding sites more rapidly in the column. A prolonged breakthrough curve was attained by a reduced inlet concentration, representing the possibility to treat a higher volume of solution. The lower concentration gradient resulted in slower transport because of a reduction in mass transfer coefficient or diffusion coefficient (Biswas & Mishra, 2015).

Fig. 3. The preliminary concentration versus breakthrough (flow rates 20 mLmin⁻¹; bed depth 5cm)

3.3.2. The impacts of NRs bed height

Fig. 4 represents the breakthrough curve achieved for adsorbing 4-NP over NRs for 3 different bed height of 5, 10, and 15 cm (38.49, 76.98, and 115.47 g of NRs) at constant 4-NP inlet concentration of 2 mgL⁻¹ and 4-NP feed flow rate of 20 mLmin⁻¹. As can be seen from **Fig. 4**, the exhaustion time (t_e) and breakthrough time (t_b) increased by increasing the bed height. The plots show that by varying the bed depth, the gradient and shape of the breakthrough curves slightly vary. At higher bed height, a larger uptake was found owing to the increased quantity of the NRs providing further fixations of the cations by active binding sites. The mass transfer zone is augmented by increasing bed height. In a column, the mass transfer zone travels from the bed entrance toward the exit. Therefore, for the fixed bed system and similar influent concentration, the increased bed height would make the long-distance for moving the mass transfer zone toward the exit leading to a prolonged breakthrough time. For larger bed depths, the increased adsorbent mass offers a greater service area increasing the volume of the treated solution (Ramesh, Gandhimathi, Nidheesh, Badabhagani, & Bharathi, n.d.).

Fig. 4. The impact of bed depth on the breakthrough curve (flow rate: 20 mLmin⁻¹ and concentration: 2mgL⁻¹)

3.3.3. The impact of feed flow rate

The impact of feed flow rate on adsorbing 4-NP over NRs was studied by changing the feed flow rate (5, 10, and 20 mLmin⁻¹) with the 4-NP concentration of 2 mgL⁻¹ and a constant adsorbent bed height of 5 cm (**Fig. 5**). According to the breakthrough curve, at relatively high flow rates, the adsorption zone rapidly reached the top of the column, indicating the quick saturation of the column. The lower flow rate led to higher contact time and a shallow adsorption zone. Less adsorption uptake was obtained at a higher flow rate, by a steeper curve with comparatively less exhaustion time and early breakthrough.

Fig. 5. The impact of flow rate on the breakthrough curve (concentration: 2mgL⁻¹ and bed depth: 5 cm)

3.3.4. Column dynamics study

The 4-NP's sorption behavior in the column was analyzed using Adams-Bohart, Thomas, and Yoon-Nelson models. The initial parameters of the models are concentration ratio, $C_t/C_0 > 0.1$ as a 10% breakthrough until $C_t/C_0 > 0.90$, and 90% breakthrough for 4-NP through a column's operation limit of mass transfer zone (Lin, Huang, Qi, Xiong, & Huang, 2017; Rafati, Ehrampoush, Rafati, Mokhtari, & Mahvi, 2019).

3.3.4.1. Thomas model

Thomas's model is based on the Langmuir kinetics of adsorption-desorption without any axial dispersion. It describes that the rate-driving force follows the second-order reversible reaction kinetics (Biswas & Mishra, 2015; Charumathi & Das, 2012). The model is linearized as:

$$\ln \ln \left(\frac{C_0}{C_t} - 1 \right) = \frac{k_{Th} q_0 m}{Q} - k_{Th} C_0 t \quad (1)$$

Where k_{Th} represents the Thomas kinetic coefficient ($\text{mLmin}^{-1}\text{mg}^{-1}$), t shows the overall flow time (min), and Q indicates the volumetric flow rate (mLmin^{-1}). The mass of the adsorbent and adsorption capacity is represented as (g) and q_0 (mgg^{-1}), respectively. The plot of $\ln[(C_0/C_t) - 1]$ versus t provides the value of q_0 and k_{Th} represented in **Table 2**.

The obtained values indicate the increase in q_0 values by increasing the influent concentration; however, by incrementing the bed depth, the q_0 values decline. Conversely, k_{Th} reduces by increasing the concentration and flow rate while it increases by increasing the bed depth. R^2 value is within the range of 0.85-0.98, indicating the acceptable fitting between the model and the empirical breakthrough curve.

3.3.4.2. Yoon-Nelson Model

The breakthrough performance of 4-NP on NRs was investigated using a simple theoretical model provided by Yoon-Nelson. The model hypothesizes that the reduction rate in the adsorption probability for each adsorbate molecule is proportionate to the adsorbate adsorption probability and the adsorbate breakthrough probability on the adsorbent (Biswas & Mishra, 2015). The model is linearized for a single-component system as:

$$\ln \left(\frac{C_t}{C_0 - C_t} \right) = k_{YN} t - \tau k_{YN} \quad (3)$$

Where τ is the time needed for 50% adsorbate breakthrough (min), k_{YN} represents the rate constant (min^{-1}), and t shows the sampling time (min). The values of k_{YN} and τ are obtained by drawing the plot of the graph between $\ln(C_t/(C_0 - C_t))$ and t (Table 4).

It was found that the values of k_{YN} reduced by decreasing the bed height while the equivalent values of τ increased by the higher bed height; τ and k_{YN} declined by increasing the primary cation concentration; and k_{YN} increased but τ reduced by increasing the flow rate. For column mode sorption, there was a similar trend for the sorption of 4-NP. **Table 2** represents the τ and k_{YN} values and other statistical parameters.

3.3.4.3. Adams-Bohart model

This model is based on the surface reaction theory assuming an instantaneous equilibrium. Hence, the adsorption rate was proportionate to the NRs' residual capacity and the 4-NP concentration. The model can be mathematically expressed as Eq. (2) (Song et al., 2015):

$$\ln \left(\frac{C_t}{C_0} \right) = k_{AB} C_0 t - k_{AB} N_0 \left(\frac{Z}{U_0} \right) \quad (2)$$

Where C_0 and C_t denote influent and effluent concentrations (mg L^{-1}), respectively. N_0 represents the saturation concentration (mg L^{-1}), k_{AB} shows the kinetic constant ($\text{L mg}^{-1}\text{min}^{-1}$), t is the flow time (min), U_0 shows the superficial velocity (cm min^{-1}), and Z is the bed depth of the fixed-bed column (cm). To obtain the values of R^2 , k_{AB} , and N_0 , the plot of $\ln(C_t/C_0)$ versus t is used. **Table 2** represents the values of k_{AB} , R^2 , and N_0 .

This method estimates the features like the mass transfer coefficient (k_{AB}) and the highest adsorption capacity (N_0). The linear plots of $\ln(C_t/C_0)$ were drawn against time t at various flow rates, initial cation concentrations, and bed heights (figures are not presented). The intercept and slope of the linear curves give the saturation concentration (N_0) and mass transfer coefficient (k_{AB}), respectively (**Table 2**). Meanwhile, a comprehensive and simple method was obtained by the Adams-Bohart model to evaluate column dynamics with the validity restricted to the used condition range. Therefore, the less applicability of this model is reflected by the poor correlation coefficient (Asmaly et al., 2015). **Table 2** shows the experimental uptake capacity and mass transfer coefficient alongside the N_0 and k_{AB} and other statistical parameters. In this table, the mass transfer coefficient increases by incrementing the flow rate and bed height while it declines by the primary concentration. This indicated that the external mass transfer dominates the total system kinetics. Nevertheless, the sorption capacity N_0 increased by the increased primary concentration, flow rate, and bed height (Chowdhury, Zain, Rashid, Ra, & Khalid, 2013).

By the incremented flow rate and concentration, k_{AB} values were reduced, however, the increased bed depth raised them.

The performance of the adsorption column at various flow rates was studied. By reducing the flow rate from 5 to 20 mLmin^{-1} , the exhaustion time and constant inlet breakthrough time were increased for 4-NP adsorption onto NRs (**Fig. 5**). This result is consistent with the results reported by other researchers (Mondal, 2009). The

contact time of the adsorbate with adsorbent was reduced by an increase in flow rate, leading to a reduction in the service time of the bed and adsorption capacity.

The breakthrough curves were attained at various bed depths (5, 10, and 15 cm) with a constant influent concentration of 2 mgL⁻¹ and a flow rate of 20 mLmin⁻¹ (**Fig. 4**). It can be seen that the exhaustion time and breakthrough time incremented by the increase in bed depth. Based on **Table 2**, by increasing the bed depth, the adsorption capacity is also increased at a 10% breakthrough, which is in line with the results reported in (Mondal, 2009). No sufficient time exists for 4-NP at the lowest bed depth for diffusing into the NRs holes. The concentration of 4-NP significantly affects the breakthrough curve (**Fig. 5**). Based on the curves, it is demonstrated that by increasing the primary 4-NP concentration, the exhaustion time and breakthrough time are declined. Based on the empirical results in **Table 2**, by increasing the concentration from 0.5 to 2 mgL⁻¹, the adsorption capacity increased. The outcomes are consistent with those of other researchers (Naveen & Malik, 2019).

3.3.4.4. Error function analysis

The most effective optimization technique is the error function analysis to investigate the best-fitted model for the investigational data. The studied models were evaluated by applying two common error functions: χ^2 and RMSE (Baghdadi, 2017):

$$RMSE = \sqrt{\frac{1}{n-p} \sum_{i=1}^n (Y_{exp} - Y_{cal})^2} \quad (7)$$

$$\chi^2 = \sum_{i=1}^n \left[\frac{(Y_{exp} - Y_{cal})^2}{Y_{cal}} \right] \quad (8)$$

where p shows the number of parameters, n represents the experimental data number, Y_{cal} shows the calculated data, and Y_{exp} is the experimental outcomes (Jafari, Rahimi, Ghaedi, Javadian, & Asfaram, 2017). Table 4 presents the error function results indicating the Thomas model as the best-fitted model for the current adsorption system.

Table 4. Parameters of Thomas, Adams-Bohart and Yoon-Nelson models for 4-NP adsorption and error function values

Condition				Thomas model				Adams-Bohart model				Yoon-Nelson model			
C0	F	Z	W	kTh×10-3	q0	R2	RSME	X2	kAB×10-4	N0	R2	RSME	X2	kYN×10-3	TYN
mg/L	mL/min	cm	gr	l/min	mg/g				L/mg.min	mg/L				l/min	min
0.5	20.0	5.0	38.5	14.6	131.3	1.0	0.1	0.8	67.4	343.4	0.9	0.2	-21.1	0.0	3.7
1.0	20.0	5.0	38.5	15.1	0.0	1.0	0.2	1.5	42.9	320.4	0.9	0.4	1.1	0.0	2.5
2.0	20.0	5.0	38.5	21.3	52.4	1.0	0.2	0.4	49.1	216.6	1.0	5.5	29.5	0.0	2.1
2.0	5.0	5.0	38.5	10.7	52.3	1.0	0.6	1.2	44.0	141.3	0.9	10.6	1.4	0.0	4.3
2.0	10.0	5.0	38.5	11.0	0.0	1.0	0.3	0.5	39.1	221.4	0.9	1.3	1.9	0.0	3.1
2.0	20.0	5.0	38.5	21.3	52.4	1.0	0.2	0.4	49.1	216.6	1.0	1.3	3.1	0.0	2.1
2.0	20.0	10.0	77.0	17.0	0.0	1.0	1.3	1.3	45.0	175.3	0.9	2.8	2.2	0.0	3.2
2.0	20.0	15.0	115.5	6.8	113.1	1.0	0.1	0.5	35.2	267.8	0.8	21.6	1.4	0.0	4.4

3.4. Regenerating the adsorbent

Regeneration is a very imperative parameter specifying the cost-effectiveness of an adsorbent (Qu, Alvarez, & Li, 2013). Due to the high cost of the nano-adsorbent, the desorption of 4-NP from the NRs surface is a key step. To regenerate the adsorbent, 5 gr of adsorbent was added to 100 mL of 4-NP solution (2 mgL⁻¹) and agitated for 20 min by a magnetic stirrer and the residue of 4-NP in solution was determined by HPLC. Then the adsorbent was washed with methanol to remove the adsorbates from the surface of the adsorbent, and they were used again. After the replication of this procedure up to 7 times, the value of q_e decreased from 0.32 to 0.16 mgg⁻¹ (**Fig.7.**). This reduction could be owing to the incomplete desorption of the 4-NP from the NRs surface. Based on a previous study (Su & Lu, 2007), "it is anticipated that the unit cost of the nano-adsorbent can decrease more in the future. Hence, nano adsorbents can be possibly profitable adsorbents.

Fig. 7. Regeneration and removal efficiency of 4-NP adsorption

4. Conclusions

This paper concludes that removing 4-NP in a packed-bed system utilizing NRs is a feasible and effective technique. The nano-adsorbent synthesized in this research was produced through the pyrolysis of the waste leachate film on silicon at 700°C. The column performance and the 4-NP adsorption capacity were highly affected by influent concentration, flow rate, and bed depth. The breakthrough time prolongs by a greater bed depth, a lower influent concentration, and a lower flow rate. The adsorption capacities were high at the flow rate of 15 mL.min⁻¹, the influent concentration of 30 mg L⁻¹, and a bed depth of 7 cm. The column adsorption process is associated with the highest adsorption capacity of 38.56 mg g⁻¹. The break was predicted through curves plotted using the Adams-Bohart, Yoon-Nelson, and Thomas models. Nevertheless, the Thomas model predicted the total breakthrough curve best. This assessment showed that the obtained NRs from garbage leachate were promising materials for removing 4-NP from contaminated water using a fixed-bed sorption column. At a constant concentration, larger bed height, and a lower feed flow rate, the column provides better performance. The empirical data obeyed the Langmuir isotherm. Furthermore, the best consistency was between the experimental column data and Yoon-Nelson and Thomas models. The adsorbed 4-NP was desorbed using methanol and the adsorbent was frequently utilized without considerable sorption capacity loss, reflecting the feasibility for commercial use.

Abbreviations:

MPs :	Micropollutants
BPA :	Bisphenol A
4-OP :	4-Octylphenol
4-NP :	4-Nonylphenol
NPs :	Nonylphenols
NOM :	Natural organic material
NRs :	Carbon nanorods
UT :	University of Tehran

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Conflict of interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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