Environmental Engineering and Management Journal

March 2020, Vol. 19, No. 3, 467-474 http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu



"Gheorghe Asachi" Technical University of lasi, Romania



FIXED-BED COLUMN STUDY OF DIAZINON ADSORPTION ON THE CROSS-LINKED CHITOSAN/CARBON NANOTUBE

Tahere Taghizade Firozjaee*, Naser Mehrdadi, Majid Baghdadi, Gholamreza Nabi Bidhendi

School of Environment, College of Engineering, University of Tehran, Tehran, Iran

Abstract

Adsorption of diazinon from aqueous solution was studied by using cross-linked Chitosan/Carbon Nanotube (CHN-CNT) in a fixedbed column. The cross linked CHN-CNT with 2.5% of MWCNT was prepared with a protected crosslinking method. The effects of the initial concentration of diazinon, bed-height, and flow rate on the adsorption of diazinon onto the cross linked CHN-CNT were investigated. The highest bed capacity of 29.47 mg/g was obtained at the initial concentration of 50 mg/L, flow rate of 10.5 mL/min, and fixed bed-height of 4 cm. Three models, namely Bohart–Adams, Thomas, and Yoon–Nelson, were investigated to predict the breakthrough curves and to determine the characteristic parameters. The experimental data were well fitted with the Yoon–Nelson model, indicating that it was suitable for continuous adsorption of diazinon onto cross-linked CHN-CNT in a fixedbed column. The findings of this study revealed that the cross-linked CHN-CNT not only has a simple synthesis method and good strength but also adsorbs the diazinon well.

Key words: adsorption, carbon nanotube, chitosan, diazinon, fixed-bed column

Received: April, 2019; Revised final: June, 2019; Accepted: October, 2019; Published in final edited form: March, 2020

1. Introduction

Pesticides have been the necessary part of agriculture field to protect plants from pest, fungi, and weeds in recent years. Despite their usefulness, concern about their overuse and potential risks to food safety, the environment, and all living organisms are increasing (Firozjaee et al., 2018). Diazinon [O, Odiethyl O-(2-isopropyl-6-methyl pyrimidin-4-yl) thiophosphate] is an organophosphorus pesticide used to control a wide range of insecticidal activity. Diazinon is considered to be of moderate toxicity compared to other organophosphates. The primary toxic effect of diazinon in humans and animals is the inhibition of acetylcholinesterase (Katsumata et al., 2008, Mirsoleimani-azizi et al., 2018). Diazinon is widely used pesticide and often is found in surface and groundwater. According to the Drinking Water Directive, pesticide concentration in drinking water should be below 0.1 μ g/L (Dolan et al., 2013). Therefore, because of their toxic and carcinogenic nature of pesticide, their removal from the environment is quite significant as well as the reduction of pesticide use (Aksakal, 2018; Farmany et al., 2016; Sorlini et al., 2019).

Adsorption technology is currently being used extensively for the removal of various types of pesticides. Among the different adsorbents, chitosan with its unique properties, such as non-toxicity, biodegradability, and biocompatibility, has a wide range of applications in water and wastewater fields (Bhatnagar and Sillanpää, 2009). Chitosan is obtained

^{*} Author to whom all correspondence should be addressed: e-mail: taghizade.eng@gmail.com and t.taghizade@ut.ac.ir; Phone: +98 21 61113171; Fax: 1417853111

by partial N-deacetylation of chitin, the second most abundant natural polymer (only after cellulose) on the earth.

Chitosan, as a polymer containing cationic amino groups, can easily adsorb anionic organic compound strongly by electrostatic attraction (Ngah et al., 2011). Chitosan can be used as an adsorbent to remove various kinds of organic pollutant due to the presence of amino and hydroxyl groups, which can serve as active sites (Bhatnagar and Sillanpää, 2009). In spite of the wide range of chitosan application, its mechanical properties are not good (Aryaei et al., 2014, Wang et al., 2005).

For improving the physical/chemical properties of chitosan, incorporation with mineral fillers is an efficient technique. Calcium phosphate cement, hydroxyapatite, and clay are mineral fillers that are often used to reinforce the chitosan matrix (Kim et al., 2004, Wang et al., 2004, Wang et al., 2005). Recently, incorporation of carbon nanotube with chitosan as a promising reinforcing filler has attracted great attention.

The studies show the cross-linked CHN-CNT composites have significant enhancement of mechanical properties compared with neat chitosan (Aryaei et al., 2014, Carson et al., 2009, Chatterjee et al., 2010, Popuri et al., 2014, Wang et al., 2005).

In this work, we studied the adsorption of diazinon on cross-linked CHN-CNT in the fixed-bed column from an aqueous solution. This study has the following objectives:

• To synthesize the Cross-linked CHN-CNT with good strength.

• To determine the best model to predict the characteristics of the fixed bed column including the capacity of adsorption, breakthrough curve and depth of the adsorption zone according to the operating parameters (initial concentration, flow rates, bed depth). For this purpose, we tested the most widely used models (Bohart-Adams, Thomas, and Yoon-Nelson) with a critical approach.

2. Materials and methods

2.1. Materials

Pristine multi-wall CNTs were purchased from Nanosav Company (Tehran Province, Iran). According to the data obtained from the company, the length of multi-wall carbon nanotube (MWCNT) was <10 μ m, the amount of amorphous carbon was <5%. The outer diameter range was from 10 to 30 nm, which was synthesized by the special chemical vapor deposition (CVD) method using iron, cobalt, and molybdenum as the catalyst.

Medium molecular weight chitosan (MMWC) powder was purchased from Sigma-Aldrich. Diazinon was also obtained from Sigma-Aldrich. A stock solution (1000 mg/L diazinon) was prepared by dissolving the appropriate amount of the diazinon in deionized water and kept in a refrigerator at 4 °C until use. All of the other reagents, nitric acid (Synth, 65%), acetic acid (Synth, 99%), Glutaraldehyde (Synth, 25%), methanol (Synth, 99.9%) were purchased from Merck.

2.2. Fixed bed column experiments

The fixed-bed column experiments were carried out at room temperature in a Pyrex glass tube with 25 cm height and 1.5 cm inside diameter. At the top and bottom of the column, a layer of glass wool was attached. A known quantity of cross-linked CHN-CNT of 0.7-1 mm particle size was packed in the column to obtain the bed height of the adsorbent of 4,6 and 8 cm. The diazinon solution in initial centration, 10, 30, and 50 mg/L, were pumped upward through the column at the desired flow rate of 10.5 and 12.4 mL/min, controlled by a peristaltic pump. Samples were taken at constant time intervals and filtered by cellulose acetate filter with 0.20 μ m pore size to prepare solutions before injection to HPLC.

2.3. Analysis

Scanning electron microscopy (DSM-960A, Zeiss) was used to study the morphology of CHN and cross-linked CHN-CNT. The concentration of diazinon was determined using HPLC (Agilent 1100 Series) with C18 column ($250 \times 4.6 \times 5$ mm) and a UV detector at a wavelength of 248 nm. The mobile phase was a mixture of acetonitrile and water with a volumetric ratio of 65/35 with an injection flow rate of 1 mL/min. Ultrasound bath (HWASHIN, Powersonic 420, 50HZ, 700 W, Seoul, Korea) was used for solution dispersion.

2.4. Preparation of the CHN-CNT adsorbent:

For preparations of the cross-linked CHN-CNT, firstly CNT was oxidized. Acidic oxidation methods have been widely reported as an effective method to purify and functionalize the surface of carbon nanotubes (CNTs) (Aviles et al., 2009, Datsyuk et al., 2008, Rosca et al., 2005). For oxidation of CNTs, 4 g of pristine CNT was dispersed in 150 mL of HNO₃ (Synth, 65%) for periods of time (5 h) and at the temperature of 140 °C. Then, it was centrifuged for 10 min at 5000 rpm. The solid residue was washed with deionized water to remove the excess nitric acid. Finally, it was dried under vacuum for 72 h.

After CNT was oxidized, the cross-linked CHN-CNT adsorbent was prepared as follows (Firozjaee et al., 2017): 50 mg of CNT was suspended in 40 mL deionized water. MWCNT suspension was homogenized in the ultrasonic bath for 90 min at 35 °C. CS solution was separately made by dissolving 2.5 gr of CS into 100 mL of deionized water and 1.5 mL of 1% acetic acid.

Using a magnetic stirrer, CS solution was completely mixed for 24 h. The MWCNT suspension was added to the CS solution in two stages and homogenized in the ultrasonic bath for 60 min at 35° to get a final weight ratio of CNTs to CS was 2.5%. A with

coagulation solution bath ($H_2O/MeOH /NaOH 4: 5: 1 w/w/w$) was made at room temperature.

decanted at a 1 rpm flow rate through a 0.2-mmdiameter syringe into a coagulation solution bath. The

granules were formed in the coagulation solution bath

and were washed several times with deionized water.

a protected-crosslinking method

glutaraldehyde was used. Cross-linking agents do not

only stabilize chitosan in acid solutions, so it improves

its mechanical properties (Chiou et al., 2004, Jin et al.,

2004, Ngah et al., 2002, Zheng et al., 2000). The

reaction was carried out by the immersion of granular

adsorbent in 25% glutaraldehyde solution at room temperature for 24 h. Then granular adsorbent was

washed several times with deionized water. Finally, it

was dried under vacuum for 72 h. The diagram of the

cross-linked CHN-CNT composite synthesis as

illustrated in Fig 1. At the first stage, acid treatment of

CNT removed impurities and bounded functional

bonding between the functionalized MWNTs and

chitosan was formed. At the third stage, the

crosslinking was performed though C=N bond

formation between the amine groups of CHN and the

Then, at the second stage, hydrogen and amine

groups carboxyl on CNT (Skandari et al., 2016).

Then

Then the prepared dispersed solution was

3. Results and discussion

3.1. Characterization of adsorbent

3.1.1. Morphological study

Fig. 2 gives the SEM images of CHN, oxidized MWCNT, and cross-linked CHN-CNT composite. Fig. 2(a) and 2(b) show the uniform surface of the CHN and the bundle of structure on the oxidized MWCNT, respectively. The surface of the cross-linked CHN-CNT composite has been exhibit in two scales in Fig. 2(c) and 2(d). According to Fig. 2(c), the surface of the cross-linked CHN-CNT display a non-uniform dispersion of MWCNTs on the chitosan surface including CNT fibers that is different from the surface of the pristine chitosan.

Some researcher showed that the cross-linked chitosan beads using glutaraldehyde have more heterogeneity on the surface compared to the chitosan beads (Ngah et al., 2002, Poon et al., 2014). In the composite of cross-linked CHN-CNT, the electrostatic interaction between the negatively charged of CNTs and the positively charged polycation of CHN is induced that cause the CNT bundles to wrap the CNTs in polymer chains. (Shawky et al., 2011).



Fig. 1. Schematic diagram of the cross-linked CHN-CNT composite synthesis





Fig. 2. SEM image of (a) Pristine chitosan; (b) oxidized MWCNT; (c) and (d) cross-linked CHN-CNT

3.1.2. Fourier Transform Infrared (FTIR) analysis

FTIR spectra of CHN and CHN–CNT are shown in Fig. 3. A major application of FTIR is to identify specific groups of molecules. The FTIR spectra of pure chitosan (a spectrum) exhibit bands at 3545 cm⁻¹ and 3379 cm⁻¹ due to the stretching vibration mode of O–H and N–H groups. The peaks at 2936 cm⁻¹ is typical of C–H stretch vibration, while the band at 1652 cm⁻¹ is due to the amide group (C=O stretching of N-acetyl groups), 1366 cm⁻¹ peak is due to the COO– group in carboxylic acid salt, 1026 cm⁻¹ stretching vibration of C–O–C in glucose circle (Chiou et al., 2004).

Two new peaks appeared at the FTIR spectra of the CHN–CNT beads at 1714 cm⁻¹ and 1568 cm⁻¹ were due to (C=O stretching of N-acetyl groups) and the COO– groups, respectively. Due to the presence of the oxidized CNTs in CHN–CNT, the stretching vibration of functional groups including C–O and C=O increased.

3.2. Fixed-bed adsorption studies

The dynamic behavior of the column was studied in the form of breakthrough (BT) curve by varying the initial concentration, bed height, and flow rate. The breakthrough curve for a column is defined by plotting the ratio of the C_e/C_0 (Ce and C_0 are the diazinon concentration of effluent and inlet, respectively) as a function of time (t) or volume of effluent (V_{eff}) for a given bed height (h). The volume of solution passed into the column V_{eff} (mL) can be calculated using Eq. (1):

$$V_{eff} = Qt_{tot} \tag{1}$$

where Q (ml/min) is the flow rate. The breakthrough and the exhaustion point were taken as the position at which $C_t/C_0 = 0.05$ and $C_t/C_0 = 0.95$, respectively (Dolatyari et al., 2018). The time taken for effluent concentration to reach the breakthrough point is known as breakthrough time.



Fig. 3. FTIR spectra of CNT and cross-linked CHN-CNT

3.2.1. Effect of the initial concentration of diazinon

To study the effect of the initial concentration of diazinon on the behavior of the column breakthrough, three different concentrations of diazinon 10, 30, and 50 mg/L, with a solution flow rate of 10 mL/min and the cross-linked CHN-CNT bed height of 4 cm were considered. According to Fig. 4(a), as the initial concentration of diazinon increased, the sharper BT curves, the faster the break-point, and the earlier the saturation of the fixed bed were observed. As a result of the decrease in saturation and breakthrough time with the increase in the initial concentration, the volume of the diazinon solution treated decreased. The increase of diazinon concentration provided higher concentration gradients and mass transfer rates, which increased the driving force of adsorption so that the highest adsorption capacity of 29.47 mg/g was observed at the initial concentration of 50 mg/L. The adsorption of diazinon by cross-linked CHN-CNT can be due to electrostatic attractions between the anionic species of diazinon (pKa =2.6) and positively charged of the amine group in cross-linked CHN-CNT particles (Jonidi-Jafari et al., 2015, Moussavi et al., 2013). Also, due to the presence of oxidized CNT fibers on the surface of CHN-CNT, π - π interactions might also have contributed to the adsorption due to presence of the aromatic fragments (π acceptors) of diazinon and the graphene sheets (π donors) of carbon nanotubes (Chen et al., 2007, Wang et al., 2009).

3.2.2. Effect of bed height

The amount of adsorbent in the column is an effective parameter on diazinon adsorption of diazinon. The experiments were done, at three different bed heights of 4, 6, and 8 cm, at a flow rate of 10.5 mL/min and the initial concentration of 30 mg/L. The effect of bed height on the BT curves is shown in Fig. 4(b). Both breakthrough and saturation time increased with increasing bed height as a result of increasing specific surface area and binding sites available for diazinon to adsorb. In high bed height, the diazinon molecules have enough time to diffuse into the whole of the adsorbent mass, due to which increase in breakthrough time happened. Also, the volume of the diazinon solution treated increased with the increasing amount of cross-linked CHN-CNT mass in higher bed height.

3.2.3. Effect of solution flow rate

The influence of flow rate of diazinon solution on the behavior of the column breakthrough was investigated by two different flow rates of 10.5 and 12.4 mL/min with a bed height of 4 cm and initial diazinon concentration of 30 mg/L. The influence of the flow rate on the BT curves is illustrated in Fig. 4(c). The lower flow rate resulted in longer BT curves and higher exhaustion times. As the flow rate increased, the BT curve became sharper because at a high flow rate, the number of diazinon molecules that passes through the adsorbent per unit of time increased. Therefore, the interaction of diazinon molecules with the adsorbent increased and adsorbent saturation occurred in shorter time. Also, at the high flow rate, the diazinon molecules do not have enough time for diffusion into the pores of the adsorbent; hence, the adsorption capacity of the cross-linked CHN-CNT column reduced.



Fig. 4. Breakthrough curves for diazinon adsorption on cross-linked CHN/CNT at (a) different initial concentrations (bed height, 4 mg/L; flow rate, 10.5 mL/min); (b) different bed heights (diazinon initial concentration, 30 mg/L; flow rate, 10.5 mL/min); (c) different flow rates (diazinon initial concentration, 30 mg/L; bed height, 4 mL/min)

3.2.4. Breakthrough Curves Modeling

The fixed bed behavior of the column is described through the concept of Breakthrough Curves. In the design of column, time and shape of the breakthrough curve are important. Therefore, for the successful design of a fixed bed column, the estimate of the concentration-time profile for the breakthrough curve is necessary. In this study, three models, Thomas, Bohart-Adams, and Yoon-Nelson, were used to fit the experimental data obtained of column study. The Bohart-Adams model (Bohart and Adams, 1920) is based on the surface reaction theory, so that ignores the intraparticle mass transfer and the external film resistance. This model assumes that the rate of adsorption is proportional to the concentration of the adsorbing species and the residual capacity of the adsorbent (Chu, 2010). This model is used for the explanation of the initial portion of the breakthrough curve (Salman et al., 2011). The equation can be written as Eq. (2):

$$ln\frac{C_t}{C_o} = K_{AB}C_o t - \frac{K_{AB}N_o Z}{U_o}$$
(2)

where U_0 (cm/min) is the linear velocity; Z (cm) is the bed height; N_0 (mg/L) the adsorption capacity of bed; and k_{AB} (L/mg min) is the mass transfer constant.

Another frequently model to estimate the adsorption capacity and predict breakthrough curves is Thomas model (Thomas, 1944). The Thomas model uses the Langmuir isotherm and pseudo-second-order kinetic for describing equilibrium adsorption date. This model is suitable to estimate the adsorption process, with no axial dispersion. The Thomas model is expressed as Eq. (3):

$$ln(\frac{C_o - C_t}{C_t}) = \frac{K_{Th}q_oW}{Q} - \frac{K_{Th}C_oV_t}{Q}$$
(3)

where k_{Th} (L/min.g) is the Thomas rate coefficient; q_0 (mg/g) the maximum solid-phase concentration of the solute; and W (g) the mass of adsorbent within the column. By plotting ln [(C₀/C_t)-1] versus t_{tot} at a given influent concentration and flow rate, k_{Th} and q_0 values were obtained. The Yoon–Nelson model supposes that the rate of decrease of adsorption of the adsorbate molecule is due to the adsorbate adsorption and also the adsorbate breakthrough on the adsorbent(Yoon and Nelson, 1984). The Yoon–Nelson equation can be written in the following linearized form:

$$ln(\frac{C_t}{C_o - C_t}) = K_{YN}t - \tau K_{YN}$$
⁽⁴⁾

where k_{YN} (min⁻¹) is the Yoon–Nelson rate constant, and τ (min) is the time required for 50% adsorbate breakthrough. The amount of τ accommodates well to the experimental data for various conditions examined. k_{YN} and τ values determined through a plot of ln [Ct/(C0 - Ct)] versus t_{tot}.

Average relative errors (ARE, %) were used to determine the difference between experimental and calculated data (Eq. 5). The lowest value of ARE (%) indicates the best model representing the experimental data (Salman et al., 2011). ARE is expressed as Eq. (5).

$$ARE = \frac{\sum_{i=1}^{N} \left| ((C / C_0)_{exp} - (C / C_0)_{cal}) / (C / C_0)_{exp} \right|}{N} \times 100$$
(5)

where: the subscripts 'exp' and 'cal' refer to experimental and calculated values, respectively, and N is the number of measurements.

Table 1 presents the calculated parameters of the fixed-bed column for three models. Results indicate the best model representing the experimental data is the Yoon-Nelson model with ARE values of 6.29-3.65 %. According to Table 1, with a change in initial concentration, bed height, and flow rate, the value of parameters is changed. For example, as the influent concentration of diazinon increased, the values of q_0 increased, but the value of k_{Th} decreased. The reason was that with increasing initial concentration, the driving force adsorption or the concentration difference between the diazinon on the adsorbent and the diazinon in the solution increased. The results obtained in this study are in agreement with those reported in some previous studies (Albroomi et al., 2017, Marzbali and Esmaieli, 2017, Salman et al., 2011, Tan et al., 2008).

3.3. Adsorption thermodynamic

The adsorption thermodynamic of diazinon onto cross-linked CHN-CNT was studied by adopting Gibbs expression. Temperature variations of 288–318 K were used for the thermodynamic study. The Gibbs free energy of the process was determined using the following Eqs. (6-7):

Table 1. Breakthrough fitting models results for adsorption of diazinon on cross-linked CHN/CNT

Condition				Thomas				Bohart-Adams				Yoon-Nelson			
Co	Q	Ζ	W	KTh	q_{θ}	R ²	ARE	KAB	No	R ²	ARE	KYN	τ	R ²	ARE
mg/l	ml/min	ст	gr	<i>Lmin⁻¹mg⁻¹</i> ×10 ⁻³	mg/g		(%)	<i>Lmin⁻¹mg⁻¹</i> ×10 ⁻³	mg/l		(%)	1/min×10 ⁻³	min		(%)
10	10.5	4	3.54	1.35	9.63	0.992	3.7	1.37	5049.2	0.935	21.73	13.3	323.2	0.996	3.65
30	10.5	4	3.54	0.517	21.23	0.994	4.63	0.516	11782.7	0.949	20.78	16.2	240.8	0.995	4.33
50	10.5	4	3.54	0.366	29.47	0.990	6.42	0.414	15046.1	0.925	20.24	19.2	201.5	0.991	6.29
30	10.5	8	7.01	0.23	26.63	0.992	5.33	0.29	12788.2	0.926	24.67	6.6	584.8	0.995	3.91
30	10.5	6	5.43	0.32	23.2	0.993	5.88	0.38	12133.2	0.931	22.7	10.3	397.2	0.994	5.64
30	12.4	4	3.54	0.63	18.88	0.991	4.19	0.62	10700.1	0.937	20.11	19.7	176	0.992	5.63

$$\Delta G^{\circ} = -RT.lnK_{c} \tag{6}$$

$$\frac{\Delta H^{\circ}}{RT} - \frac{\Delta S^{\circ}}{R} = -\ln K_c \tag{7}$$

where ΔG° is the Gibbs free energy change (KJ/mol); ΔH° is the standard enthalpy change (KJ/mol); ΔS° is the standard entropy change (J/mol K); K_c is the thermodynamic equilibrium constant of adsorption (L/gr); R is the gas constant (8.314 J/(K.mol)); and T is the absolute temperature (K). The values of ΔH° and ΔS° are computed from the slope and intercept of the plot (Fig. 5). The plot of lnK_c verses 1/T gives a straight line with a coefficient of determination (R²) of 0.97 for diazinon, as shown in Fig. 5.



Fig. 5. The plot of ln k_c vs. 1/T for estimation of thermodynamic parameters for adsorption of diazinon on cross-linked CHN-CNT

The thermodynamic adsorption parameters are summarized in Table 2. The negative values of ΔG° in all temperatures revealed that the adsorption was a fairly favorable and spontaneous process. Also, the decrease in ΔG° by the increase in temperatures confirmed that high temperatures would make the adsorption of diazinon onto cross-linked CHN-CNT more spontaneous and faster. In other words, high temperatures are favorable (Moussavi et al., 2013). The positive value of ΔH° (28.9 kJ/mol) revealed that the adsorption of diazinon onto cross-linked CHN-CNT increased with an increase in temperature and is endothermic in nature. The values of standard entropy change ΔS° (111 J/mol K) suggested that the degree of dispersion and randomness of the process increased with temperature rise.

5. Conclusions

The present study demonstrated the ability of cross-linked CHN-CNT to remove diazinon from

aqueous solution in a fixed-bed column.

The results of morphology tests revealed the bonding of the carbon nanotubes and chitosan was successful. The change in initial concentration, bed height, and flow rate influenced the amount of diazinon adsorbed. The adsorption models were applied to evaluate the performance of the fixed bed column and predict the breakthrough curves.

The experimental data showed that the Yoon-Nelson model described the behavior of adsorption of diazinon onto cross-linked CHN-CNT in a fixed-bed column better than Thomas and Bohart-Adams models. According to obtained results, it seems that the cross linked CHN-CNT, as an effective and inexpensive adsorbent, can be able to use for pesticide removal in large-scale adsorption column.

References

- Albroomi H., Elsayed M., Baraka A., Abdelmaged M., (2017), Batch and fixed-bed adsorption of tartrazine azo-dye onto activated carbon prepared from apricot stones, *Applied Water Science*, 7, 2063-2074.
- Aksakal O., (2018), Effects of alpha-cypermethrin pesticide on DNA stability and oxidative enzymes in maize (Zea mays), *Environmental Engineering and Management Journal*, **17**, 435-442.
- Aryaei A., Jayatissa A.H., Jayasuriya A.C., (2014), Mechanical and biological properties of chitosan/carbon nanotube nanocomposite films, *Journal of Biomedical Materials Research Part A*, **102**, 2704-2712.
- Aviles F., Cauich-Rodriuez J., Moo-Tah L., May-Pat A., Vargas-Coronado R., (2009), Evaluation of mild acid oxidation treatments for MWCNT functionalization, *Carbon*, 47, 2970-2975.
- Bhatnagar A., Sillanpää M., (2009), Applications of chitinand chitosan-derivatives for the detoxification of water and wastewater-a short review, Advances in Colloid and Interface Science, 152, 26-38.
- Bohart G., Adams E., (1920), Some aspects of the behavior of charcoal with respect to chlorine, *Journal of the American Chemical Society*, 42, 523-544.
- Carson L., Kelly-Brown C., Stewart M., Oki A., Regisford G., Luo Z., Bakhmutov V.I., (2009), Synthesis and characterization of chitosan-carbon nanotube composites, *Materials Letters*, 63, 617-620.
- Chatterjee S., Lee M.W., Woo S.H., (2010), Adsorption of congo red by chitosan hydrogel beads impregnated with carbon nanotubes, *Bioresource Technology*, **101**, 1800-1806.
- Chen W., Duan L., Zhu D., (2007), Adsorption of polar and nonpolar organic chemicals to carbon nanotubes, *Environmental Science & Technology*, **41**, 8295-8300.
- Chiou M.-S., Ho P.-Y., Li H.-Y., (2004), Adsorption of anionic dyes in acid solutions using chemically crosslinked chitosan beads, *Dyes and Pigments*, **60**, 69-84.

Table 2. Thermodynamic parameters for diazinon adsorption onto cross-linked CHN-CNT

4 Ja 4	Thermodynamic		D ²				
Aasorbeni	parameters	318	308	<i>298</i>	288	Λ-	
CHN-CNT	$\Delta G^{\circ}(KJ/mol)$	-2.88	-4.35	-5.39	-6.21	0.976	
	$\Delta H^{\circ}(KJ/mol)$	28.9					
	$\Delta S^{\circ}(J/(moL.K))$	111					

- Chu K.H., (2010), Fixed bed sorption: setting the record straight on the Bohart-Adams and Thomas models, *Journal of Hazardous Materials*, **177**, 1006-1012.
- Datsyuk V., Kalyva M., Papagelis K., Parthenios J., Tasis D., Siokou A., Kallitsis I., Galiotis C., (2008), Chemical oxidation of multiwalled carbon nanotubes, *Carbon*, 46, 833-840.
- Dolan T., Howsam P., Parsons D.J., Whelan M.J., (2013), Is the EU drinking water directive standard for pesticides in drinking water consistent with the precautionary principle?, *Environmental Science & Technology*, **47**, 4999-5006.
- Dolatyari L., Yaftian M.R., Rostamnia S., (2018), Adsorption of Th (IV) and U (VI) on functionalized SBA-15 mesoporous silica materials using fixed bed column method; breakthrough curves prediction and modeling, *Separation Science and Technology*, 53, 1282-1294.
- Farmany A., Mortazavi S.S., Mahdavi H., (2016), Ultrasond-assisted synthesis of Fe₃O₄/SiO₂ core/shell with enhanced adsorption capacity for diazinon removal, *Journal of Magnetism and Magnetic Materials*, 416, 75-80.
- Firozjaee T.T., Mehrdadi N., Baghdadi M., Bidhendi G.N., (2017), The removal of diazinon from aqueous solution by chitosan/carbon nanotube adsorbent, *Desalination* and Water Treatment, **79**, 291-300.
- Firozjaee T.T., Mehrdadi N., Baghdadi M., Nabi Bidhendi G., (2018), Application of nanotechnology in pesticides removal from aqueous solutions - A review, *International Journal of Nanoscience and Nanotechnology*, 14, 43-56.
- Jin J., Song M., Hourston D., (2004), Novel chitosan-based films cross-linked by genipin with improved physical properties, *Biomacromolecules*, 5, 162-168.
- Jonidi-Jafari A., Shirzad-Siboni M., Yang J.-K., Naimi-Joubani M., Farrokhi M., (2015), Photocatalytic degradation of diazinon with illuminated ZnO–TiO 2 composite, *Journal of the Taiwan Institute of Chemical Engineers*, 50, 100-107.
- Katsumata H., Matsumoto T., Kaneco S., Suzuki T., Ohta K., (2008), Preconcentration of diazinon using multiwalled carbon nanotubes as solid-phase extraction adsorbents, *Microchemical Journal*, **88**, 82-86.
- Kim S.B., Kim Y.J., Yoon T.L., Park S.A., Cho I.H., Kim E.J., Kim I.A., Shin J.-W., (2004), The characteristics of a hydroxyapatite-chitosan-PMMA bone cement, *Biomaterials*, 25, 5715-5723.
- Marzbali M.H., Esmaieli M., (2017), Fixed bed adsorption of tetracycline on a mesoporous activated carbon: Experimental study and neuro-fuzzy modeling, *Journal* of Applied Research and Technology, **15**, 454-463.
- Mirsoleimani-azizi S.M., Setoodeh P., Samimi F., Shadmehr J., Hamedi N., Rahimpour M.R., (2018), Diazinon removal from aqueous media by mesoporous MIL-101 (Cr) in a continuous fixed-bed system, *Journal of Environmental Chemical Engineering*, 6, 4653-4664.
- Moussavi G., Hosseini H., Alahabadi A., (2013), The investigation of diazinon pesticide removal from contaminated water by adsorption onto NH₄Cl-induced activated carbon, *Chemical Engineering Journal*, **214**, 172-179.
- Ngah W.W., Endud C., Mayanar R., (2002), Removal of copper (II) ions from aqueous solution onto chitosan

and cross-linked chitosan beads, *Reactive and Functional Polymers*, **50**, 181-190.

- Ngah W.W., Teong L., Hanafiah M., (2011), Adsorption of dyes and heavy metal ions by chitosan composites: A review, *Carbohydrate Polymers*, **83**, 1446-1456.
- Poon L., Younus S., Wilson L.D., (2014), Adsorption study of an organo-arsenical with chitosan-based sorbents, *Journal of Colloid and Interface Science*, **420**, 136-144.
- Popuri S.R., Frederick R., Chang C.-Y., Fang S.-S., Wang C.-C., Lee L.-C., (2014), Removal of copper (II) ions from aqueous solutions onto chitosan/carbon nanotubes composite sorbent, *Desalination and Water Treatment*, 52, 691-701.
- Rosca I.D., Watari F., Uo M., Akasaka T., (2005), Oxidation of multiwalled carbon nanotubes by nitric acid, *Carbon*, 43, 3124-3131.
- Salman J., Njoku V., Hameed B., (2011), Batch and fixedbed adsorption of 2, 4-dichlorophenoxyacetic acid onto oil palm frond activated carbon, *Chemical Engineering Journal*, **174**, 33-40.
- Shawky H.A., El-Aassar A.H.M., Abo-Zeid D.E., (2011), Chitosan/carbon nanotube composite beads: Preparation, characterization, and cost evaluation for mercury removal from wastewater of some industrial cities in Egypt, *Journal of Applied Polymer Science*, 125, E93-E101.
- Skandari S., Torabian A., Bidhendi G.N., Baghdadi M., Aminzadeh B., (2016), Preparation of engineered carbon nanotube materials and its application in water treatment for removal of hydrophobic natural organic matter, *Desalination and Water Treatment*, 57, 1-12.
- Sorlini S., Collivignarelli M.C., Miino M.C., (2019), Technologies for the control of emerging contaminants in drinking water treatment plants, *Environmental Engineering and Management Journal*, 18, 2203-2216.
- Tan I., Ahmad A., Hameed B., (2008), Adsorption of basic dye using activated carbon prepared from oil palm shell: batch and fixed bed studies, *Desalination*, 225, 13-28.
- Thomas H.C., (1944), Heterogeneous ion exchange in a flowing system, *Journal of the American Chemical Society*, **66**, 1664-1666.
- Wang J., De Boer J., De Groot K., (2004), Preparation and characterization of electrodeposited calcium phosphate/chitosan coating on Ti6Al4V plates, *Journal* of Dental Research, 83, 296-301.
- Wang S.-F., Shen L., Zhang W.-D., Tong Y.-J., (2005), Preparation and mechanical properties of chitosan/carbon nanotubes composites, *Biomacromolecules*, 6, 3067-3072.
- Wang Z., Shirley M.D., Meikle S.T., Whitby R.L., Mikhalovsky S.V., (2009), The surface acidity of acid oxidised multi-walled carbon nanotubes and the influence of in-situ generated fulvic acids on their stability in aqueous dispersions, *Carbon*, 47, 73-79.
- Yoon Y.H., Nelson J.H., (1984), Application of gas adsorption kinetics I. A theoretical model for respirator cartridge service life, *American Industrial Hygiene Association Journal*, **45**, 509-516.
- Zheng H., Du Y.-M., Yu J.-H., Xiao L., (2000), The properties and preparation of crosslinked chitosan films, *Chemical Journal of Chinese Universities -Chinese Edition*, 21, 812-814.