

# Carboxylated carbon nanotubes as an efficient and cost-effective adsorbent for sustainable removal of insecticide fenvalerate from contaminated solutions

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Received: 10 February 2016 / Accepted: 21 September 2016 / Published online: 3 October 2016  
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**Abstract** In this study, carboxylic multiwall carbon nanotubes (CMNTs) were used as an adsorbent for removing fenvalerate as a toxic insecticide from solution through batch experiments. The influence of four independent parameters of HCl, initial fenvalerate concentration, CMNTs dosage, and contact time on the fenvalerate adsorption process was investigated. Raman spectroscopy and thermogravimetric analysis confirmed that the adsorption and maximum adsorption capacity ( $40.0 \text{ mg g}^{-1}$ ) showed high adsorption potential of the proposed sorbent. The kinetic, isothermic, and thermodynamic of fenvalerate adsorption on CMNTs were evaluated to better understand this environmental friendly adsorption strategy. A pseudo-first-order kinetic described very well the experimental data of the adsorption kinetics. The experimental data found to be properly fitted to Freundlich model, which indicates that the sorption takes place on a heterogeneous material. The thermodynamic results showed the negative value of the standard free energy ( $\Delta G^0$ ) and standard enthalpy change ( $\Delta H^0$ ) showing an exothermic and spontaneous system. Repeated availability of adsorbent investigated and SEM and HRTEM of reused adsorbent showed stability and non-aggregatable attributes of CMNTs.

**Keywords** Nanoadsorbent · Adsorption · Water treatments · Carbon nanotubes

## Introduction

Water pollution is a global menace in these days due to the agriculture activities, urbanization, and heavy industrialization, and the magnitude of it is enhancing significantly. Hence, providing clean water and a clean environment for people is the most important matter [1]. Over the last 30 years, synthetic pyrethroids, such as fenvalerate, cyfluthrin, and deltamethrin, have been widely used as agricultural, home insecticides to replace the more toxic and environmentally persistent organochlorine and organophosphorous pesticide. However, in these days, one of the key reasons of pollution in surface and ground waters is using the large scale of insecticides and pesticides in agriculture. Due to extensive use, safe, efficient, and economic strategies for their elimination were attracted so much attention [2]. In this, hence, the nanoparticles can play major roles for the treatment of natural waters, soils, sediments, industrial, and domestic waste water.

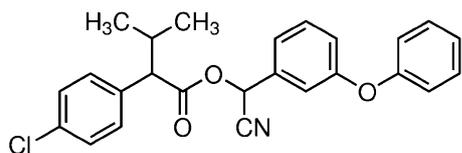
Carbon nanotubes (CNTs) gained great importance on account of their wide range applications in field emission, conducting plastics, conductive adhesive, structure materials [3–7]. CNTs have also shown the *efficiency potential* in the removal of widespread range of chemical contaminants such as aromatic solutes due to their special shape with high external surface area [8–11]. It should be noted that the movement of CNTs in solution is high, and the all volume can be quickly scanned with little amounts of nanoparticles [12–15]. Therefore, using nanoadsorbent could be resolved or greatly diminished the current problems involving water quality.

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**Scheme 1** The structure of fenvalerate

We recently reported the removal of polycyclic aromatic hydrocarbons, in particular, pyrene and related aromatic hydrocarbons by mild catalytic method and also friendly environmental oxidation of alcohols to aldehydes and ketons using a novel dimer copper complex at the present of green oxidants, such as  $\text{H}_2\text{O}_2$  and *t*-butyl hydrogen peroxide [16–18]. In continuing our work, the CMNTs were used in the removal of fenvalerate as one dangerous insecticide, and it was provided greater sensitivity, lower cost, and shorter turn-around times in removal of insecticides (Scheme 1).

## Experimental

Analytical grade fenvalerate for the experiment was purchased from Fluka Co. (Germany). A fenvalerate stock solution was prepared in ethanol and kept in a refrigerator at 4 °C until use. All other chemicals were purchased from Merck Co. (Germany). Thermo SCIENTIFIC model NICOLET iS10 spectrophotometer was used for IR spectra of adsorbent in the 4000–400  $\text{cm}^{-1}$  regions. HRTEM (Philips CM30) and SEM (Shimadzu 50, model s4160) analysis was performed for checking the morphology of the products. TGA (Shimadzu 50) were employed for considering the removal process. UV–Vis (Cary 100 UV spectrophotometer) was recorded the spectra of fenvalerate.

## Results and discussions

### Fenvalerate adsorption studies

Adsorption of fenvalerate on HMWCNTs was investigated by UV–Vis spectrophotometry at 276 nm [19]. The effect of amount of HCl, initial fenvalerate concentration, contact time, and the dosage of CMNTs was considered by batch adsorption experiments at room temperature (25 °C). For each experiment, 10 mL of fenvalerate stock (5 mg/l) was added to Erlenmeyer flasks at room temperature. For each experiment, 10 ml of fenvalerate stock (5 mg/l) was added to Erlenmeyer flasks. Samples were conducted at predetermined time of contact (10, 20, 30, 40, 50, 60, and 70 min) and filtered through 0.25\_μm filters. The concentration of residual fenvalerate was analyzed by UV–Vis

spectrophotometry after filtering. Fenvalerate uptake by *S. cerevisiae* was determined according to:

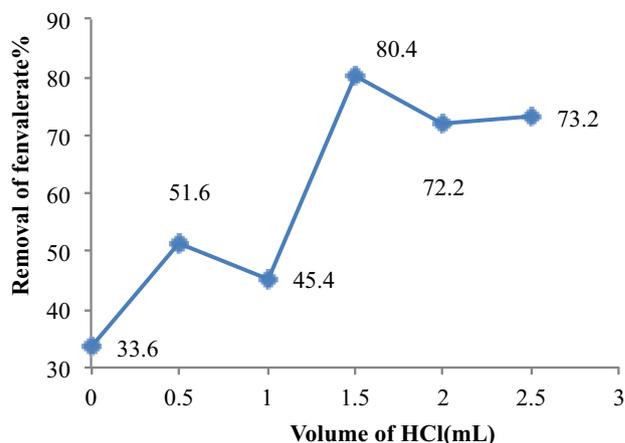
$$q_e = \frac{(C_0 - C_e)V}{m}, \quad (1)$$

where  $q$  (fenvalerate uptake) is the concentration of adsorbed fenvalerate on the CMNTs (mg/g),  $V$  is the amount of fenvalerate in contact with the CMNTs (mL),  $C_0$  is the initial,  $C_e$  is equilibrium (residual) concentration of fenvalerate (mg/L), respectively, and  $m$  is the amount of CMNTs adding to solution (g) [20]. Percentage of removal fenvalerate contacting with the CMNTs was determined according to:

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

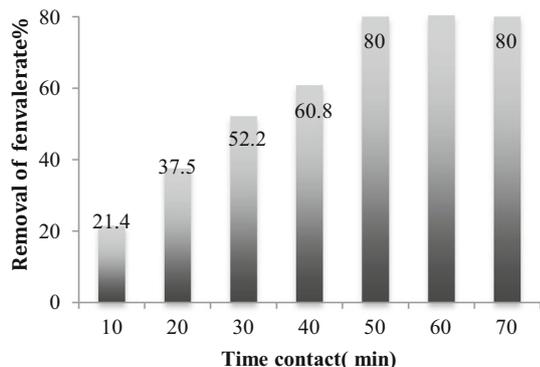
### Optimization of fenvalerate removal strategy

To understand better fenvalerate removal, the effect of increasing amount of HCl(0.1 N) on removal percentage is shown in Fig. 1. Because of the electrostatic interactions between the fenvalerate molecules and the CMNTs surface, the obtained optimum value was more than 1.5 mL of HCl (0.1 N). It should be noted that fenvalerate was hydrolyzed at alkaline media; therefore, just the acid media were checked. It has already been known that there are some oxygen groups, such as carboxylic groups (–COOH) and hydroxylic groups (–OH), on the surface of CNTs. The water molecules adsorbed to the oxygen groups on carbon surface become secondary adsorption centers, which retain other water molecules by means of hydrogen bonds. It can also be suggested that because more oxygen groups on the surface of CNTs ionize, more water is adsorbed by these groups at lower pH values. Thus, when water cluster forms on these oxygen groups, the adsorption is affected in two



**Fig. 1** The effect of HCl volume on the fenvalerate removal by CMNTs





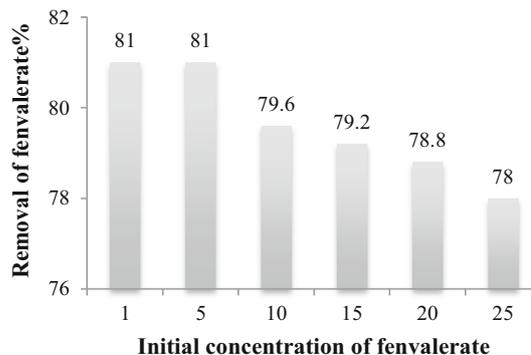
**Fig. 2** The effect of time contact on fenvalerate removal by CMNTs<sup>a</sup>

ways. First, since these oxygen groups are located on the surface of CNTs, the formation of water cluster hinders access to the surface. A second possible influence of water adsorption is interference with surface carboxylic groups. These groups can adsorb organics through donor–acceptor complex formation. The formation of water cluster on carboxylic groups is suspected to block adsorption on the carboxylic sites [21]. If water cluster is indeed the cause of the decreased capacity observed at lower pH, it is to expect that the effect would be reduced if the number of oxygen groups on the surface of CNTs were reduced.

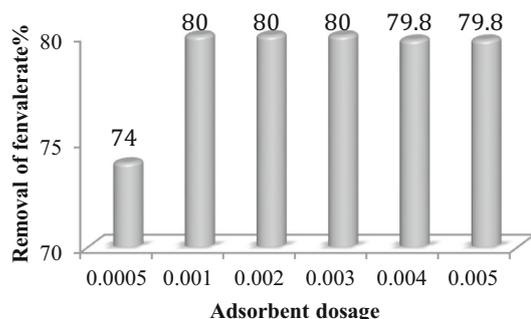
The contact time of fenvalerate and CMNTs was investigated in this adsorption system [22]. In contrast, by increasing the contact time, the amount of fenvalerate adsorbed on the CMNTs was increased. Fifty minutes was required for CMNTs to adsorb fenvalerate (see Fig. 2). CMNTs do not have porous structure as traditional adsorbents such as activated carbon and to have equilibrium, and the adsorbate has to move from the exterior surface to the inner surface of the pores. Therefore, the short time needed suggesting that CMNTs have very high efficiencies potential to remove fenvalerate from contaminated water.

The effect of initial concentration of fenvalerate on adsorption by CMNTs was investigated (Fig. 3). At 25 °C with changing initial fenvalerate concentration from approximately 1–25 mg L<sup>-1</sup>, the fenvalerate amount sorbed decreased from 81 to 78 mg g<sup>-1</sup>. Percent fenvalerate removal was higher at low fenvalerate concentrations at the present of CMNTs, due to availability of unoccupied binding sites on the sorbents. Percent fenvalerate removal diminished with increasing dye concentration because of nearly complete coverage of the binding sites of each CMNT at high fenvalerate concentrations.

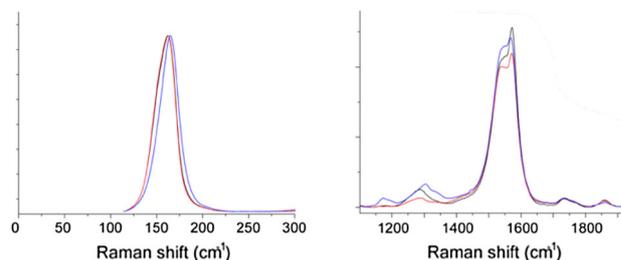
The effect of CMNTs dosage on fenvalerate uptake was also considered (Fig. 4). By increasing the amount of CMNTs from 1.0 to 5.0 mg/L, the removal of fenvalerate was increased and its optimum value was 1 mg/L. It should be noted that using of more than 1 mg/L of CMNTs was not economical. The availability of more adsorption sites



**Fig. 3** The effect of initial concentration of fenvalerate on removal of it by CMNTs



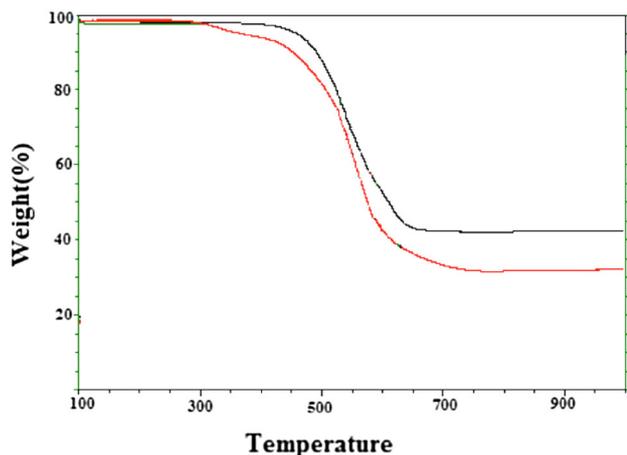
**Fig. 4** The effect of mount of CMNTs as adsorbent on removal of fenvalerate



**Fig. 5** The Raman of CMNTs before adsorption (blue), after adsorption (black), after two times reused (red)

of CMNTs and surface area was enhanced by increasing adsorbent dosage [23].

The adsorption of fenvalerate on CMNTs was considered by Raman spectroscopy and thermogravimetric analysis (TGA). The Raman spectra of CMNTs and adsorbed fenvalerate on CMNTs are compared in Fig. 4 ( $\lambda_{exc} = 785$  nm). The two spectra are very similar, thus proving that the structure of the nanotubes is preserved upon modification with no increase in the relative intensity of the D band (Fig. 5), while the left shift of G band, after adsorption, is in agreement with previous reports for the noncovalent modification of CMNTs with fenvalerate [24]. The radial breathing modes (RBM) had small right shift. On the other hand, thermogravimetric analysis (TGA) of



**Fig. 6** TGA of CMNTs before and after adsorption of fenvalerate

the fenvalerate absorbed on CMNTs was shown a weight loss of 4 % at approximately 325 °C. The TGA results were shown that 40 mgr of fenvalerate was absorbed on one gr of CMNTs showing very well that 80 % of fenvalerate was removed by CMNTs (Fig. 6).

### Isotherm adsorption

Freundlich and Temkin isotherms were shown the adsorption behavior of fenvalerate onto CMNTs. In fact, Freundlich equation was explained the equilibrium adsorption, which is most commonly written as [26–29]:

$$\ln q_e = \ln k_f + (1/n) \ln C_e, \quad (3)$$

where the equilibrium adsorption capacity of the CMNTs is  $q_e$  (mg fenvalerate/g CMNTs), the equilibrium concentration of fenvalerate is  $C_e$  (mg/L), and sorption capacity and intensity are  $K_f$  (mg/L) and  $1/n$ , respectively.

The effects of indirect adsorbate/adsorbate interactions on adsorption isotherms were considered by Temkin and Pyzhev. The heat of adsorption of all molecules in the layer would decrease linearly with coverage due to adsorbate/adsorbate interactions. This isotherm can be shown as:

$$q_e = RT \ln(AC_e)/b, \quad (4)$$

where the Temkin isotherm constant is  $A$  ( $L g^{-1}$ ), the gas constant is  $R$  ( $8.314 J mol^{-1} K^{-1}$ ), the heat of adsorption is Temkin constant ( $J mol^{-1}$ ), and the absolute temperature is  $T$  (K) [25–27]. The linear form of Temkin isotherm is as follow:

$$q_e = B \ln A + B \ln C_e, \quad (5)$$

where  $B = RT/b$  [24–26].  $A$  and  $B$  constants can be determined by plotting  $q_e$  against  $\ln C_e$  (Table 1).

The result of the curve was fitted with Freundlich equation (Table 2) and was not fitted with Temkin equation, because the value of  $R^2$  in this isotherm is higher than

**Table 1** Freundlich equation and Temkin equation constants

Freundlich isotherms		Temkin isotherms	
$1/n$	0.96161	$A_T$	3.78
$K_f$	38.9	$B_T$	52.831
$R^2$	0.9997	$R^2$	0.8457

1.5 mL HCl 0.1 M; fenvalerate:  $5 mg L^{-1}$ ; CMNTs: 0.0010 g; contact time: 50 min

**Table 2** The effect of temperature and thermodynamic parameters of the fenvalerate adsorption on the CMNTs at different temperatures

$T$ (K)	$\Delta G^0$ ( $kJ mol^{-1}$ )	$\Delta H^0$ ( $kJ mol^{-1}$ )	$\Delta S^0$ ( $J mol^{-1} K^{-1}$ )
308	8.219		
318	7.059	40.273	104.2
328	6.135		

1.5 mL HCl 0.1 M; fenvalerate:  $5 mg L^{-1}$ ; CMNTs: 0.0010 g; contact time: 50 min

the other one ( $R^2 = 0.96161$ ). Fitting the results with Freundlich model reflected heterogeneous surface and adsorption into a porous material. Therefore, this system seemed to be porous adsorption.

### Kinetic modeling and thermodynamic of adsorption

The kinetics of fenvalerate adsorption onto CMNTs to evaluate the controlling mechanism of adsorption process using two simplified kinetic models including the Lagergren pseudo-first order and pseudo-second order, as follows:

$$q_t/dt = k_1(q_e - q_t), \quad (6)$$

where  $k_1$  is the adsorption rate constant of the pseudo-first-order model,  $q_t$  is the amount of fenvalerate adsorbed at time  $t$  (mg/g), and  $q_e$  is the amount of fenvalerate adsorbed at equilibrium (mg/g).

The pseudo-second-order kinetic model can be represented in the following form:

$$dq_t/dt = k_2(q_e - q_t)^2, \quad (7)$$

where  $k_2$  is the pseudo-second-order rate constant ( $g/mg \text{ min}$ ), at time  $t$  (mg/g),  $q_t$  is the amount of fenvalerate adsorbed, and at equilibrium,  $q_e$  is the amount of the fenvalerate adsorbed (mg/g).

From the slope and the intercept of the plots of  $t$  versus  $t/q$ , the  $k_2$  and  $q_e$  values of the pseudo-second-order kinetic model can be obtained, respectively (Fig. 7) [28]. The adsorption capacity of fenvalerate onto CMNTs at a certain time ( $q_t$ ,  $mg g^{-1}$ ) and the adsorption capacity of

fenvalerate onto CMNTs at equilibrium ( $q_e$ ,  $\text{mg g}^{-1}$ ) can be calculated by the following equations:

$$q_t = V \frac{C_0 - C_t}{m} \tag{8}$$

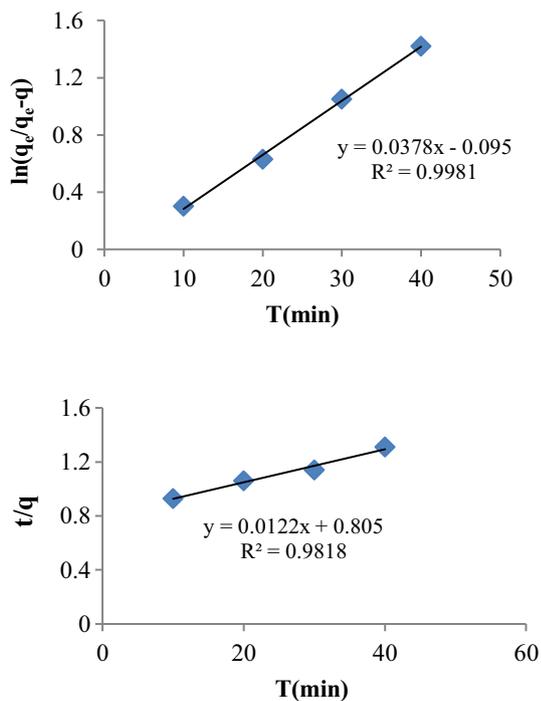
$$q_e = V \frac{C_0 - C_e}{m}, \tag{9}$$

where the fenvalerate initial concentration is  $C_0$  ( $\text{mg/L}$ ), the fenvalerate equilibrium concentration is  $C_e$  ( $\text{mg/L}$ ), the fenvalerate concentrations  $C_t$  ( $\text{mg/L}$ ) at time  $t$ , the solution volume is  $V$  ( $\text{L}$ ), and the CMNTs mass is  $m$  ( $\text{g}$ ) [29]. The kinetic parameters, such as  $k_1$  (the pseudo-first-order rate constant) and  $k_2$  (the pseudo-second-order rate constant),  $q_{e,\text{cal}}$  (calculated equilibrium adsorption amount), and  $q_{e,\text{exp}}$  (experimental equilibrium adsorption amount), and regression coefficients ( $R^2$ ) are shown in Fig. 6. The correlation coefficients ( $R^2$ ) and comparing the values of  $q_{e,\text{cal}}$

and  $q_{e,\text{exp}}$  were shown the conformity between experimental data and the model predicted values. The relative higher value of  $R^2$  and the lower value of  $\Delta q$  are the more applicable model to the kinetics of fenvalerate adsorption onto CMNTs. The pseudo-first-order model has the higher value of  $R^2$  and the lower value of  $\Delta q$  (Fig. 6). Thus, the pseudo-first-order kinetic model was described very well the fenvalerate adsorption onto CMNTs. This founding indicates that adsorption capacity is proportional to the active sites number of CMNTs.

On the other hand, the effect of temperature on fenvalerate adsorption onto CMNTs was investigated at the range of 308–328 °K. The equilibrium adsorption of fenvalerate was plotted against the temperature, as shown in Table 3. The amount of equilibrium adsorption of fenvalerate decreased with the increasing temperature from 308 to 328 °K that indicates an exothermic process. In fact, by increasing the temperature, a tendency for the target molecules is to escape from the solid phase to the bulk phase. Negative  $H^0$  value ( $-40.273 \text{ kJ/mol}$ ) was indicated that the whole process is exothermic. The standard sorption entropy  $S^0$  ( $-104.2 \text{ kJ/mol}$ ) is negative too, and the fixation of fenvalerate resulted in the decrease in the freedom of the whole system. However, some process like ion-exchange will release water molecule from solid surface into bulk solution which increase the entropy. Therefore, the entropy alteration is the sum of these two processes. Temperature was affected directly on standard free energy ( $G^0$ ), and it can change at different temperatures. Here, at all temperatures,  $G^0$  is negative, and this proposed adsorption system is spontaneous in nature, and the spontaneity decreases with the increase in temperature (Table 2) [30, 31].

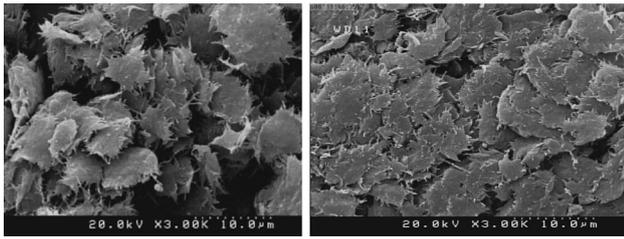
One of the properties of our advanced adsorbent is the recoverability of it, which will significantly reduce the cost of proposed adsorption system showing that CMNTs are a good candidate for using in water and wastewater treatment at high scale. In this regard, for this purpose as a part of the study, probability for recycling of CMNTs was investigated by TEM and SEM of CMNTs (Figs. 8, 9). The comparisons between SEM and TEM of CMNTs, before and after reusing, were proved that the morphology, structure, and *non-aggregatable attributes* of CMNTs, after



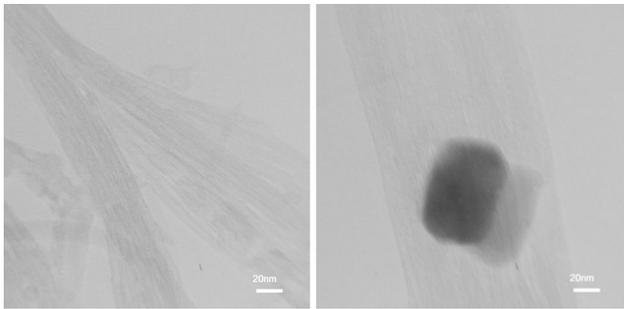
**Fig. 7** Adsorption kinetics of fenvalerate onto CMNTs. The pseudo-first order (*top*) and the pseudo-second order (*down*)

**Table 3** The effect of different sorbents on removal of fenvalerate

Sorbent	Time (h)	Sorbent dosage (g)	Sorption capacity ( $\text{mg g}^{-1}$ )
CMNTs	0.83	0.001	40
MWCNTs	8	0.2	1.12
Areca	10	0.2	4.01
Iranian natural zeolite	8	0.2	3.7
Fly ash	8	0.2	2.2
Bamboo charcoal	8	0.2	3.1



**Fig. 8** The SEM of CMNTs before (*left*) and after (*right*) adsorption



**Fig. 9** The TEM of CMNTs before (*left*) and after (*right*) adsorption

reusing, suggest that CMNTs have very high potential for fenvalerate removal from contaminated solutions.

On the other hand, different kinds of sorbents were studied. In this, hence, areca (a food waste), Iranian natural zeolite, bamboo charcoal, MWCNT, and fly ash, using for heavy metal removal [32–35], were checked as adsorbent. The obtained results were shown that the time of the proposed method is much shorter (50 min), and the amount of sorbent is significantly lower than other ones (0.001 g), which is indicative of efficiency of CMNTs (Table 3).

## Conclusion

A practical and economy method for removal of fenvalerate has been developed. The sorption capacity of studied CMNTs could be enhanced with the increase in 1.5 mL of HCl (0.1 N). The TGA results were shown that at the present of 0.001 gr of CMNTs, 80 % of fenvalerate were removed after 50 min, and Raman data was confirmed the adsorption. A pseudo-first-order rate equation was confirmed by adsorption kinetics consideration, and Freundlich isotherm was fitted by equilibrium adsorption data. The change of sorption kinetics and isotherms with the increase in temperature have similar trend. The initial sorption rate and sorption equilibrium capacity decrease with the rise in temperature from 308 to 328 K. Calculated thermodynamic parameters were shown the negative value and an exothermic and spontaneous adsorption process. Therefore, the application of CMNTs in the removal of fenvalerate was provided greater sensitivity, a lower cost,

shorter times process in environmental remediation. The comparison between the SEM and TEM of after and before adsorption was confirmed that the stability of CMNTs structure and morphology as adsorbent. The Raman of CMNTs after two times reused was not changed (Fig. 6).

**Acknowledgments** We are thankful to the University of Jiroft and Vali-e-Asr University of Rafsanjan Research Council for their support on this work.

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