Removal of caffeine from aqueous solution using multi-wall carbon nanotubes: kinetic, isotherm, and thermodynamics studies

Bahrami, M., Amiri, M.J.[*] and Koochaki, S.

Department of Water Engineering, College of Agriculture, Fasa University, Fasa, Iran

ABSTRACT: The occurrence of contaminants in wastewaters, and their behavior during wastewater treatment and production of drinking water are key issues to re-use water resources. The present research aims to remove caffeine from aqueous solutions via adsorption technique, using Multi-Wall Carbon Nanotubes (MWCNTs) as an adsorbent under different experimental conditions. The processing variables such as pH (2-12), contact time (1-30 min), initial concentration of caffeine (2-314 mg/L), temperature (25, 50, 80 °C), and adsorbent mass (0.02-0.15 g) have been investigated with equilibrium and kinetic studies on adsorption of caffeine onto MWCNTs being also developed. Maximum caffeine removal has been obtained at pH=7 and adsorption equilibrium has been achieved in 5 min. The use of pseudo second-order kinetic model with determination coefficient of 99.3% (R^2=0.993), has made the adsorption kinetics to be well fitted. The caffeine equilibrium adsorption data have been best fitted to Langmuir-Freundlich Model with a relatively high determination coefficient of 96.5% (R^2=0.965) and maximum adsorption capacity of 35.61 mg/g of caffeine on MWCNTs. The thermodynamic parameters display that the adsorption of caffeine onto MWCNTs has been non-spontaneous and endothermic in nature.

Keywords: equilibrium, MWCNTs, non-spontaneous, zdsorption.

INTRODUCTION

Caffeine ($C_8H_{10}N_4O_2$) is an alkaloid that belongs to methylxanthine family, naturally present in foods such as coffee, tea, kola nuts, and cacao beans. Inside human bodies, caffeine acts as a Central Nervous System (CNS) stimulant. Similarly, it acts as a natural pesticide for plants as it paralyzes and kills some insects, attempting to feed on the plant (Pavel et al., 2003). Caffeine is released in the surrounding water bodies and has been detected in ground water, surface water, and wastewater effluents having high concentration (~10 μg/L) (Glassmeyer et al., 2005). The literature also indicates that caffeine is toxic to most aquatic organisms (Chen et al., 2008; Pollack et al., 2009).

Various technologies have been developed to remove caffeine from wastewater, such as oxidation/reduction, biological treatment, coagulation/ flocculation, adsorption, membrane separation, and ion exchange (Ma et al., 2012). Al-Qaim et al. (2015) concluded that electrochemical oxidation treatment is a promising technique to treat organic pollutants like caffeine in tolerated samples, e.g. effluent of sewage treatment plants.

Adsorption is one of the most effective techniques, because its processing, based on this concept, is simple, highly efficient,

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[*] Corresponding author Email: mj_amiri@fasau.ac.ir

easy to operate, and usable in small scale household units. As a result, it is being widely used (Amiri et al., 2016). Adsorbents must have appropriate characteristics, such as high selectivity, high surface area and adsorption capacity, good regeneration capacity, long-lasting lifetime, and low cost (Aboul-Kassim & Simoneit 2001). Various adsorbents have been developed to remove organic pollutants such as caffeine from water (Alexander et al., 2012). Activated Carbon (AC) is the most commonly used commercial adsorbent, thanks to its excellent adsorption capacity for organic contaminants (Hosseini et al., 2011; Sotelo et al., 2012, 2014). However, it has certain drawbacks such as limited availability, low adsorption capacity, and difficult recovery.

Carbon Nanotubes (CNTs), which were discovered by Iijima (1991), are one of the most widely studied carbon nano-materials that can serve as excellent adsorbents for toxic material, owing to their hollow and layered structure along with large specific surface area (Tan et al., 2012). CNTs adsorbents can be classified into three types: Single-Wall CNTs (SWCNTs), Multi-Wall CNTs (MWCNTs), and functionalized CNTs (f-CNTs). Carbon nano-materials like MWCNTs are much more effective in removing methyl orange (MO) (Hosseini et al., 2011), arsenazo (III), methyl red (MR) (Ghaedi et al., 2011a), and Eriodirome Cyanine R (ECR) (Ghaedi et al., 2011b) from wastewater than AC.

This paper aims to investigate the effectiveness of MWCNTs in the elimination of caffeine in batch reactors. The influences of operational parameters such as initial caffeine concentration, reaction time, temperature, adsorbent mass, and initial pH have been evaluated also. Furthermore, caffeine uptake has been dealt with in terms of Freundlich, Langmuir, Langmuir–Freundlich, and Redlich-Peterson isotherms, and pseudo-first-order, pseudo-second-order, Elovich,

and fractional power adsorption kinetic models have been employed on laboratory data to obtain information concerning the interaction between caffeine and the MWCNTs.

MATERIALS AND METHODS
Caffeine (i.e 1,3,7-Trimethylpurine-2,6-dione $C_{28}H_{10}N_4O$) was purchased from Sigma–Aldrich (Steinheim, Germany), in analytical purity to be used in the experiments directly, without any further purification. Appropriate concentrations of caffeine solutions were prepared by diluting a stock solution with deionized water. As for MWCNTs (diameter: 10–20 nm, length: ~30 μm), they were obtained from Nanocyl Co. (Belgium) to be used as adsorbents. All other chemicals were purchased from Merck (Germany).

Laboratory batch experiments were carried out in order to study the adsorption of caffeine on MWCNTs. They were conducted at room temperature (25±2 °C), using several bottles under different experimental variables, including pH (2-12), reaction time (1–30 min), adsorbent mass (0.02–0.15 g), and the initial caffeine concentration (2–314 mg/L). Thermodynamic experiments, however, were conducted at three different temperatures (25, 50, and 80 °C) with the temperature being set by a LABO MS-H-S Heater. The bottles, containing the mixture of caffeine solution with MWCNTs, were shaken at 120 rpm, using a SEBD001 rotary orbital shaker. In the final stage of batch experiments, the solutions passed through filter paper no. 40 and the concentration of the residual caffeine in the remaining solution was determined, using a UV/VIS 2100S spectrophotometer. The adsorption efficiency (%R) and the adsorption capacity (q) (mg/g) of caffeine with MWCNTs were calculated by means of Equation (1) and (2), respectively.

$$\% R = \frac{C_0 - C_e}{C_0} \times 100 \tag{1}$$

$$q = \frac{C_0 - C_e}{m} \times V \qquad (2)$$

where C_0 and C_e are the initial concentration of caffeine in solution and the concentration in equilibrium (mg/ L), respectively. V is the volume of solution (L) and m the adsorbent mass (g).

To apply MWCNTs as efficient adsorbent in real environmental applications, the kinetics, isotherms, and thermodynamics of the adsorption must be well understood. Among all kinetic models, the present study used four models, which are the most usual ones, namely pseudo-first-order of Lagergern, pseudo-second-order of Ho, Fractional Power (F–P), and Elovich, in order to fit the experimental data of caffeine removal with MWCNTs. Table 1 presents all studied mathematical kinetic models, where q_e and q_t (mg/g) are the adsorption capacities at equilibrium and at time t, respectively. The parameters k_f (min^{-1}) and k_s (g/mg min) are the rate coefficients for pseudo-first-order and pseudo-second-order kinetic models, respectively; α stands for the initial adsorption rate (mg/g min), while β is desorption constant (g/mg) during any experiment. Finally, a (mg/g min^b) and b are the F–P kinetic model constants.

Table 1. Mathematical equations of the used kinetic, isotherm, and thermodynamic models

	.Kinetic models	
Model	**Equation**	**Parameter and dimension**
Pseudo first-order (Lagergern)	$q_t = q_e(1 - \exp(-k_f t))$	K_f (1/min) q_e, q_t (mg/g)
Pseudo second-order (Ho)	$q_t = \dfrac{k_s q_e^2 t}{1 + q_e k_s t}$	k_S (mg/g.min) t: time (min)
Elovich	$q_t = \left(\dfrac{1}{\beta}\right)\ln(\alpha\beta) + \left(\dfrac{1}{\beta}\right)\ln t$	α (mg/g min) β (g/mg)
Fractional power	$q_t = at^b$	a (mg/g min), b (–)
	Isotherm models	
Model	**Equation**	**PParameter and dimension**
Langmuir	$q_e = \dfrac{bq_{\max}C}{1 + bC}$	q_{max} (mg/g) b (L/mg)
Freundlich	$q_e = K_F C_e^{\frac{1}{n}}$	K_F (mg/g)(mg/L)$^{-n}$ n: model exponent (–)
Langmuir-Freundlich (L-F)	$q_e = \dfrac{q_{\max}(bC_e)^n}{1 + (bC_e)^n}$	n(–) (0<n<1)
Redlich-Peterson (R-P)	$q_e = \dfrac{K_R C_e}{1 + a_R C_e^{\beta}}$	K_{RP} (L/g) a_{RP} (L/mg) β (–) (0<β<1)
	Thermodynamic equations	
	Equation	**Parameter and dimension**
ΔS & ΔH	$\ln k_d = \dfrac{\Delta s}{R} - \dfrac{\Delta H}{RT}$	
k$_d$	$k_d = \dfrac{q_e}{Ce}$	R (314 / 8J / mol k) K_d (l/g) T (k)
ΔG	$\Delta G = -RT \ln K_d$	
E$_a$	$E_a = \Delta H + RT$	

An adsorption isotherm describes the fraction of sorbate molecules, partitioned between liquid and solid phases at the equilibrium state. Adsorption of caffeine by MWCNTs was modelled, using four widely-used isotherm models, namely Freundlich (F), Langmuir (L), Redlich-Peterson (R-P), and Langmuir-Freundlich (L-F). The Langmuir isotherm assumes monolayer adsorption on a uniform surface with a finite number of adsorption sites. Once a site is filled, no further sorption can take place there. As such, the surface will eventually reach a saturation point where the maximum adsorption of the surface has been achieved (Arshadi et al., 2014). The Freundlich isotherm is applicable to both monolayer (chemisorption) and multilayer adsorption (physisorption), being based on this assumption that the adsorbate adsorbs onto the heterogeneous surface of an adsorbent. Table 1 shows the used mathematical isotherm models, in which q is the adsorbed amount and C_e, the equilibrium concentration of caffeine. In the Langmuir model, q_{max} is the maximum solute adsorbed at the equilibrium state for a layer (mg/g) to complete, while b is a constant that depends on adsorption energy, showing the enthalpy of adsorption. It is also an index to describe the binding energy of surface adsorption. In Freundlich model, K_F and n are the coefficients, attributed to the adsorption capacity and the adsorption intensity of the adsorbent, respectively, whereas in Langmuir-Freundlich (L-F) model, b (L/mg) and n are the coefficients, attributed to the L-F equilibrium constant and the exponent of the L-F equation, respectively. K_R, a_R, and β in Redlich-Peterson (R-P) isotherm are the model constants, with K_R being the solute adsorptivity (L/g); a_R, the rate relevant to the adsorption energy (L/mg); and β, the heterogeneity constant ($0<\beta<1$).

In this study the thermodynamic parameters that assess and determine the absorption process, include standard free energy (ΔG), standard enthalpy (ΔH), and standard entropy (ΔS). Table 1 shows the used mathematical thermodynamic equations, where R (8.314 J/mol K) is universal gas constant; T, the solution temperature (K); and K_d, the ratio of adsorbed material by the adsorbent (mg/g) to the remaining materials in the solution (mg/L). The values of ΔH and ΔS are obtained from the slope and intercept of the plots of $\ln K_d$ versus $1/T$ respectively (Mobasherpour et al., 2014).

The solution pH, was adjusted with 0.1 M HCl/NaOH, having been measured by a pH-meter (Metrohm, 827 pH Lab). The pH rate of zero (pH$_{PZC}$) for the adsorbent was obtained via the solid addition method (Balistrieri & Murray 1981). Nitrogen (99.999%) adsorption experiments were carried out at -196 ℃, using a volumetric apparatus (Quantachrome NOVA automated gas sorption analyzer). All samples were degassed under the vacuum at 120 ℃ for 16 h, prior to the adsorption experiments. The concentrations of caffeine solutions were measured with a UV–Vis spectrophotometer at a wavelength, corresponding to the maximum absorbance, $\lambda_{max} = 275$ nm. The specific surface area of the adsorbent was measured, using the Brunnauer-Emmett-Teller (BET) method, while the pore size was calculated by means of the Barrett-Joyner-Halenda (BJH) method. The functional groups, present in the MWCNTs, were investigated, using the Furier transform infrared (FT-IR spectroscopy) technique, with FT-IR spectra recorded, using a Jasco FT/IR-680 plus spectrophotometer as KBr pellets. The size and surface morphology of MWCNTs were determined using scanning electron microscope (MIRA3TESCAN-XMU).

The research also assessed the goodness of the fit between estimated experimental and model data, via linear coefficient of determination (R^2) and Root mean square error (*RMSE*) as follows:

$$R^2 = \frac{\left[\sum_{i=1}^{n}(qi-\overline{q})(q\hat{i}-\overline{\hat{q}})\right]^2}{\sum_{i=1}^{n}(qi-\overline{q})^2 \sum_{i=1}^{n}(q\hat{i}-\overline{\hat{q}})} \qquad (3)$$

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n}(q_e-q_c)^2}{n}} \qquad (4)$$

where q_e and q_c are the measured and model-estimated amounts of caffeine adsorbed, respectively, and n is the number of measurements. A lower *RMSE* value and higher R^2 value have been taken into consideration to show the full agreement between measured and estimated caffeine adsorbed data.

RESULTS AND DISCUSSION

Figure 1 illustrates the surface and textural morphology of MWCNTs by SEM image. As shown in this figure, the MWCNTs' diameter range from 10 to 20 nm and they are more than 30 μm long. The well-developed porous structure can be observed in Figure 1 too, while Figure 1(a) displays quite clearly MWCNTs, though after adsorption (b), the surface is tarnished, suggesting a thin layer of caffeine covering the MWCNTs, without changing their morphology.

Figure 2 shows FTIR spectra of the adsorbent, before and after caffeine adsorption. The carbonyl band at 1637.4 cm^{-1} is the most intense one, which is related to the presence of $C{=}C$ in aromatic rings of caffeine molecules, corresponding to the stretching vibration of $C{=}O$ bonds. This peak shows caffeine adsorption on MWCNTs, according to Figure 3 (Singh et al., 1998). The broad band at 3435 cm^{-1} is characteristic of alcohol *O-H* stretch and amine *N-H* stretch groups, present in the adsorbent surface. Looking at the FTIR spectra of MWCNTs, one can see a small peak at 2927.8 cm^{-1}, assigned to the carboxylic acid *O-H* stretch and alkyl *C-H* stretch groups. These peaks show minor chemical reactions between the caffeine molecules and MWCNTs surfaces. The peak at 1402.18 cm^{-1} is characteristic of aromatic *C-H* bending.
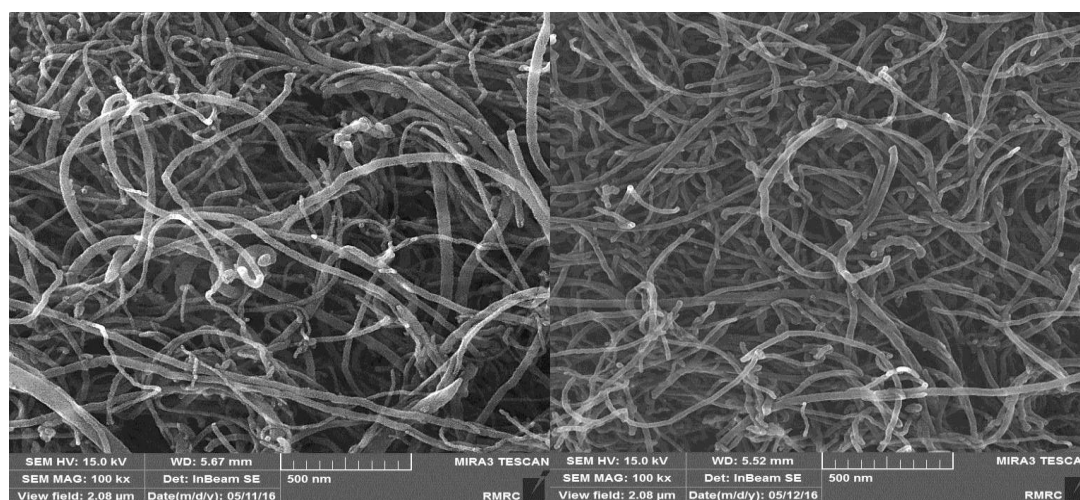
Fig. 1. SEM of MWCNTs (a) before, and (b) after caffeine adsorption
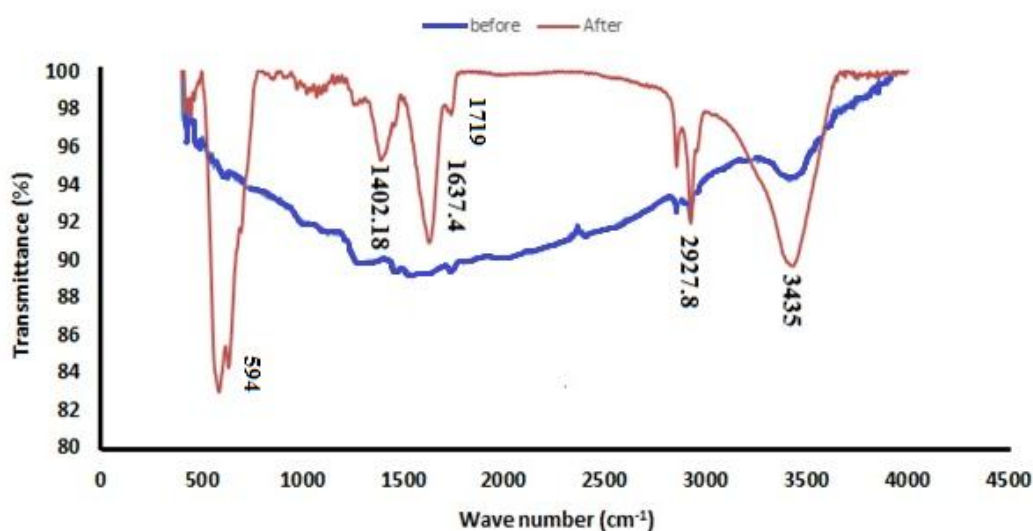
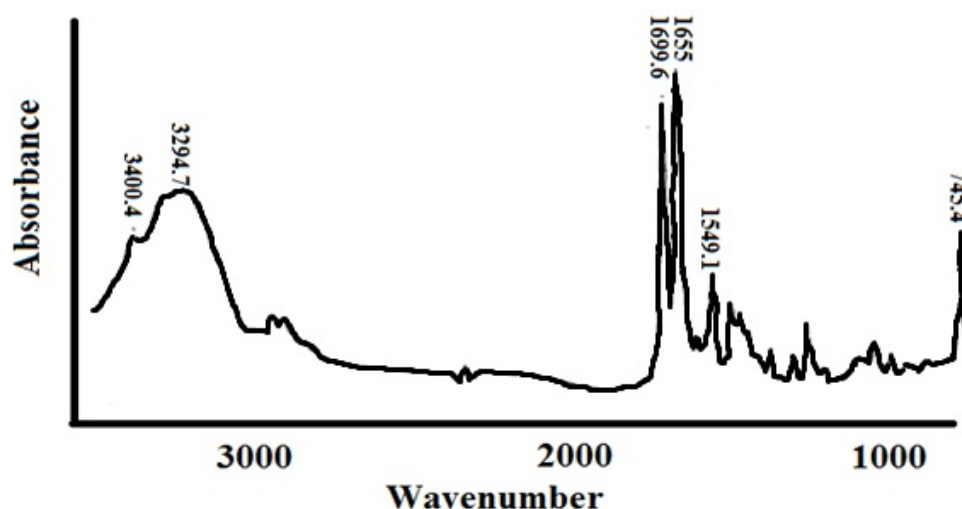**Fig. 2. FTIR spectra of MWCNTs after and before caffeine adsorption**

Fig. 3. FTIR spectra of standard caffeine recorded, using the ATR accessory (Singh et al., 1998)

The physical properties of the MWCNTs show that the surface area and mean pore diameter are 200 (m²/g) and 3.46 (nm), respectively. However, the great specific surface area and average pore size of MWCNTs suggest an increase in the approachability of active sites of the adsorbent, in contact with the contaminated water.

Figure 4 shows the percentage of caffeine, removed by MWCNTs, as a function of equilibrium solution's pH, in which the Caffeine removal efficiency of MWCNTs has been measured under different pH conditions. According to Figure 4, the removal efficiency ascended from 97% to 99% when the initial pH rose from 2 to 7, then at pH>7 removal efficiency descended as solution pH was further increased. In order to better comprehend the net charge of the adsorbent surface at different solution pHs, the point of zero charge (pH$_{ZPC}$) of the adsorbent was measured.

Figure 5 demonstrates the results of pH$_{ZPC}$ determination. ZPC is defined as the pH at which the total surface charges become zero. It was estimated that the adsorbent's

pH_{ZPC} would be about 3.82, indicating that the surface charge of the adsorbent is negative at high pHs of the solution. The adsorption dependence on pH can be due to both non-electrostatic and electrostatic interactions. In case of caffeine, its binding onto MWCNTs is mainly due to a non-electrostatic interaction, involving hydrogen bonding, which is preferred at pH<3.82 (point of zero charge), where the carbonaceous surface has a net positive charge; however, it becomes less effective on negative carbonaceous surface at pH>3.82. The solution pH determines not only the predominant species in the solution but also the net charge on the carbonaceous materials.

Ayranci et al. (2005) studied this aspect on phthalic acid and its esters adsorption onto activated carbon-cloth. Several works have been conducted to elucidate the adsorption mechanism of many molecules on different adsorbents. They reveal that adsorption of organic molecules from dilute aqueous solutions on carbon materials is a complex interplay between electrostatic and non-electrostatic interactions and that both interactions depend on the characteristics of the adsorbent as well as the adsorbate, not to mention on chemical properties of the solution, itself (Moreno-Castilla, 2004). As a similar substance, MWCNTs can be considered effective in removing organic contaminants.
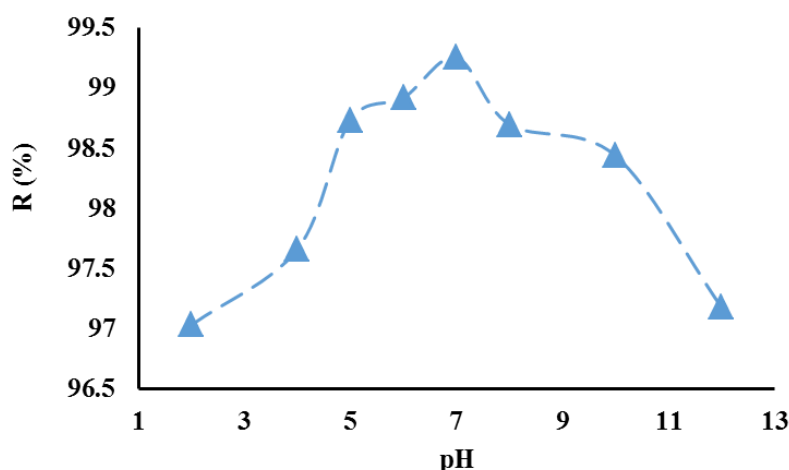

**Fig. 4. Effect of pH on caffeine adsorption by MWCNTs adsorbent
(Caffeine initial concentration 50 mg L^{-1}, adsorbent loading 0.1 g, adsorption time 30 min)**
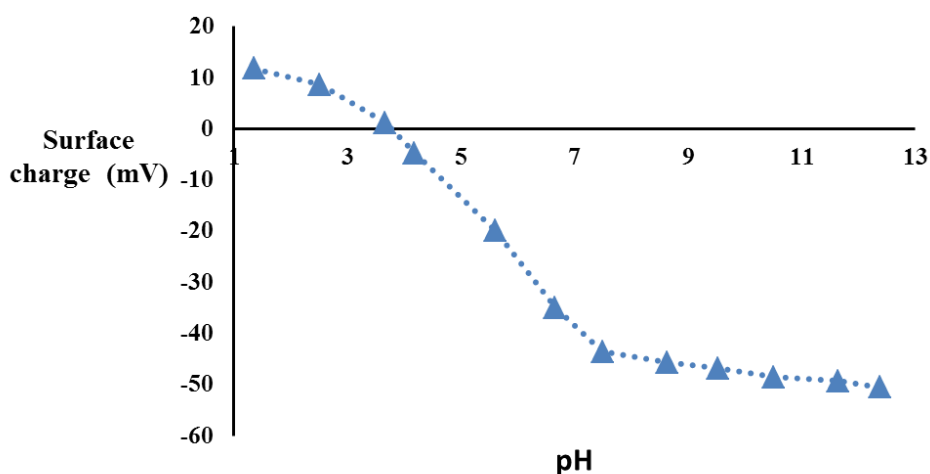

Fig. 5. Zeta potential of the adsorbent as a function of pH

In order to obtain the adsorption isotherm, batch experiments were carried out to find out the equilibrium data. Previously, experiments had been conducted at various time intervals to determine the minimum time, required to reach adsorption equilibrium. According to the results, demonstrated in Figure 6, caffeine adsorption has become steady after 5 min for. The removal efficiency increases with time during the first 5 min. Afterwards, the adsorption curve reaches a state of equilibrium after this time. According to Zeledon-Toruno et al. (2007), adsorption appears to proceed in two stages. Initially, the adsorbates are quickly adsorbed in the adsorbent macro and mesopores; afterwards, slower migration of the adsorbed compounds to less accessible sites takes place within adsorbent, allowing larger amounts of caffeine to be progressively adsorbed as the contact time increases.

Solutions of different initial caffeine concentrations (2, 5, 10, 15, 20, 25, 30, 50, 80, 100, 200, 300, 350, 400, and 413 mg/L)

were used to investigate the effect of concentration on caffeine removal by 0.1 g sorbent at pH =7. As presented in Figure 7, at first, adsorption efficiency increased as solution concentration is raised. Although the percentage of adsorption declined, MWCNTs' equilibrium adsorption capacity grew as the initial caffeine concentration was increased. At low initial solution concentration, the surface area and the availability of adsorption sites were relatively high, and the caffeine were easily adsorbed. At higher initial solution concentrations, the total available adsorption sites are limited, resulting in decreased percentage removal of caffeine. The increased q_e at higher initial concentration can be attributed to enhanced driving force. Marcal et al. (2015) studied the equilibrium adsorption as a function of equilibrium concentration. Their results showed that adsorption capacity of the adsorbent (*Organically Modified Saponites*) increased as the initial caffeine concentration was raised.
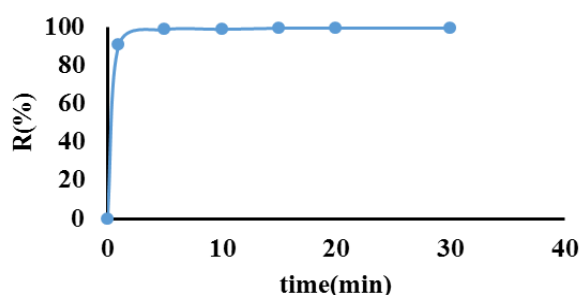

Fig. 6. Impact of contact time on caffeine adsorption by MWCNTs adsorbent (caffeine initial concentration 50 mg L^{-1}, adsorbent loading 0.1 g, pH=7)
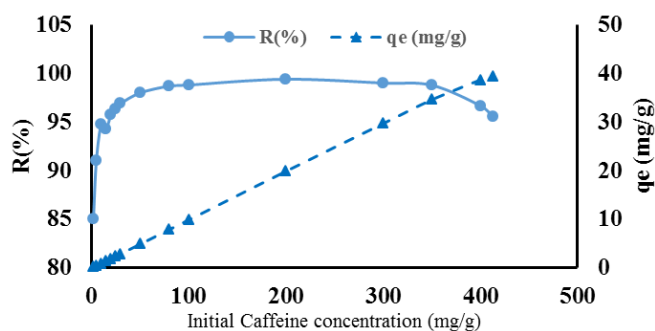

Fig. 7. Effect of initial concentration on caffeine adsorption by multi-wall CNTs adsorbent

Another variable chosen for the study of caffeine adsorption was the amount of adsorbent, which ranged between 0.1 and 0.15 g, while keeping caffeine concentration at 50 mg/L (Fig. 8). Increasing the adsorbent dosage from 0.1 to 0.15 g, raised caffeine adsorption from 59.1% to 99.7%, while decreasing the adsorption capacity from 14.7 to 3.3 mg/g. This was due to the presence of more binding sites for complexation of caffeine.

Kinetic study

Figure 9 demonstrates the fitting of experimental kinetic results with pseudo-first-order, pseudo second-order, fractional power, and Elovich models with Table 2

presenting the estimated parameters values. It can be observed that the pseudo second–order model gives the best fit with more R^2 and less *RMSE* than the pseudo first-order model but their predicted q_e values (4.99 and 4.95 mg/g) are overestimated, compared to the experimentally-observed value (4.92 mg/g). Therefore, the pseudo second-order model could be used to predict the kinetics of caffeine adsorption of MWCNTs. Alvarez et al. (2015) concluded that pseudo-second order model well described kinetic experimental data, giving a maximum adsorption capacity of 182.5 mg/g for caffeine adsorption onto a carbon xerogel, treated with urea solution.
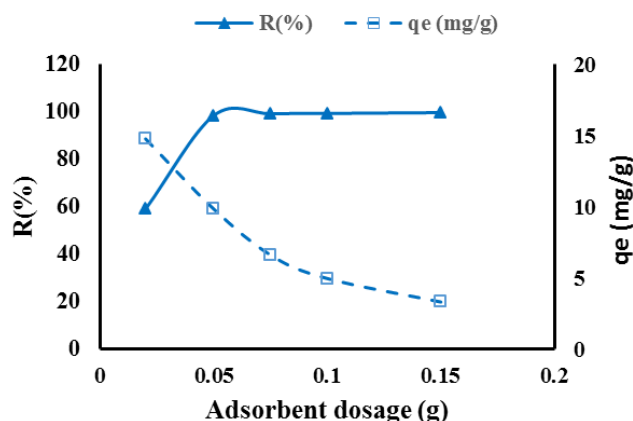

Fig. 8. Impact of adsorbent dosage on caffeine removal by multi-wall CNTs adsorbent

Table 2. The kinetic models' parameters for caffeine adsorption by MWCNTs in aqueous solution

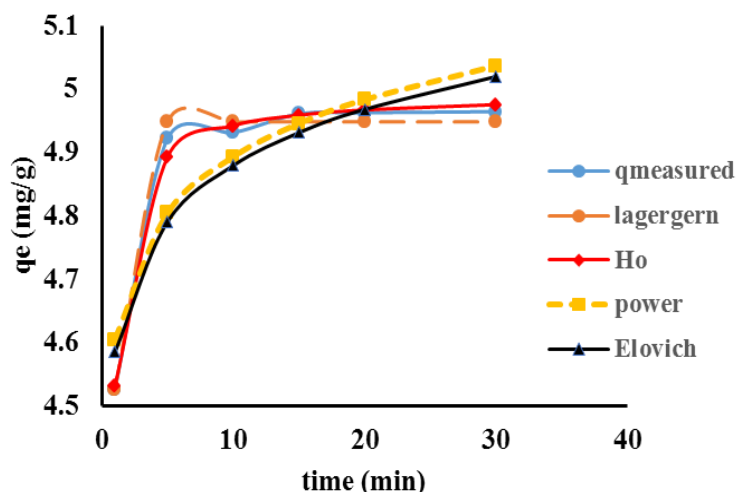| Kinetic model	Parameters	Value
Pseudo first-order (Lagergern)	K_1(1/min)	2.46
	q_e(mg/g)	4.95
	R^2	0.989
	RMSE	0.02
Pseudo second-order (Ho)	K_2(g/mg.min)	1.96
	q_e(mg/g)	4.99
	R^2	0.993
	RMSE	0.017
Fractional power	a(mg/g.min^b)	4.6
	b	0.026
	R^2	0.819
	RMSE	0.083
Elovich	α(mg/g.min)	1.07e+15
	β(g/mg)	3.38
	R^2	0.826
	RMSE	0.08

Fig. 9. The fitting of kinetic models for caffeine on MWCNTs

Table 3 presents various equilibrium contact times of caffeine adsorption, using different adsorbents. Accordingly, with regard to other equilibrium contact times, the applied adsorbent in the present study could potentially be used as a feasible and efficient adsorbent to remove caffeine from aqueous solutions in a short time period.

Figure 10 compares the fitting of the experimental data with Langmuir, Freundlich, Langmuir-Freundlich, and Redlich-Peterson adsorption isotherms, suggesting that the Langmuir-Freundlich model is more suitable to simulate the adsorption isotherm of caffeine by MWCNTs. Also, Table 4 gives a summary of related parameters. It can be seen that the Langmuir-Freundlich model possesses higher R^2 and less *RMSE* than the other models. Moreover, the maximum adsorption capacity (q_m) was 35.61 mg/g.

The parameter *n* implies an abnormality from the linearity of the adsorption process, representing the extent of non-linearity between the concentration of the adsorbate and the adsorbent as follows: if *n*<1, the adsorption process is potentially physisorption; if *n=*1, the adsorption is linear; and if *n*>1, the adsorption process is definitely chemisorption. According to the results from Table 4, we see that *n* is below 1, which shows that caffeine adsorption onto the surfaces of MWCNTs was in a favorable experimental condition, being intrinsically a physiosorption process.

Furthermore, the equilibrium adsorption capacity of caffeine onto the favored adsorbent were studied at higher temperatures of 50 and 80 ^{o}C at pH = 7 (Fig. 11). As can be in Figure 11, increasing the temperature of caffeine solutions from 25 to 50 and 80 ^{o}C caused the adsorption capacity of the adsorbent fall, which in turn suggests weak adsorption interaction between the adsorbent surface and the caffeine, thus supporting physisorption. At high temperature, the thickness of the boundary layer decreases due to the increased tendency of caffeine to escape from the adsorbent surface to the solution phase, resulting in decreased adsorption while the temperature rises (Amiri et al., 2013, 2016). As seen in Figure 11, by increasing the temperature from 25 to 80 °C, MWCNTs adsorption capacity descended from 4.96 to 4.88 mg/g.

Table 3. The equilibrium contact time of caffeine adsorption by means of various adsorbents

Adsorbent	Equilibrium contact time	Adsorption capacity	Reference
Activated carbon	3 day	270 mg/g	Sotelo et al. (2012)
Sepiolite minclear SG36	10 day	73.96 mg/g	Alvarez et al. (2013)
Trichosporon asahii	24 hr	98.9%	Lakshmi & Das (2013)
Organically modified saponites	240 min	80.54 mg/g	Marcal et al. (2015)
Carbon xerogel	48 hr	182.5 mg/g	Alvarez et al. (2015)
Commercial PAC	24 hr	12.63 mg/g	Acero et al. (2012)
SBA - 15	24 hr	$1.2 \; \mu mol/g$	Ortiz-Martinez et al. (2015)
Multi-wall carbon nanotubes	5 min	35.61 mg/g	This study

Table 4. Parameters of the equilibrium model for caffeine adsorption by MWCNTs

Isotherm model	Parameter	Value
Freundlich	$k_f (mg/g)(mg/L)^{-n}$	9.019
	n	1.79
	R^2	0.758
	$RMSE$	7.71
Langmuir	q_{max} (mg/g)	54.26
	b (L/mg)	0.206
	R^2	0.843
	$RMSE$	6.14
Langmuir-Freundlich	q_{max} (mg/g)	35.61
	b (L/mg)	0.179
	n	0.123
	R^2	0.965
	$RMSE$	3.06
Redlich-Peterson	K_R	8.808
	a_R	0.008
	β	2.062
	R^2	0.898
	$RMSE$	5.20

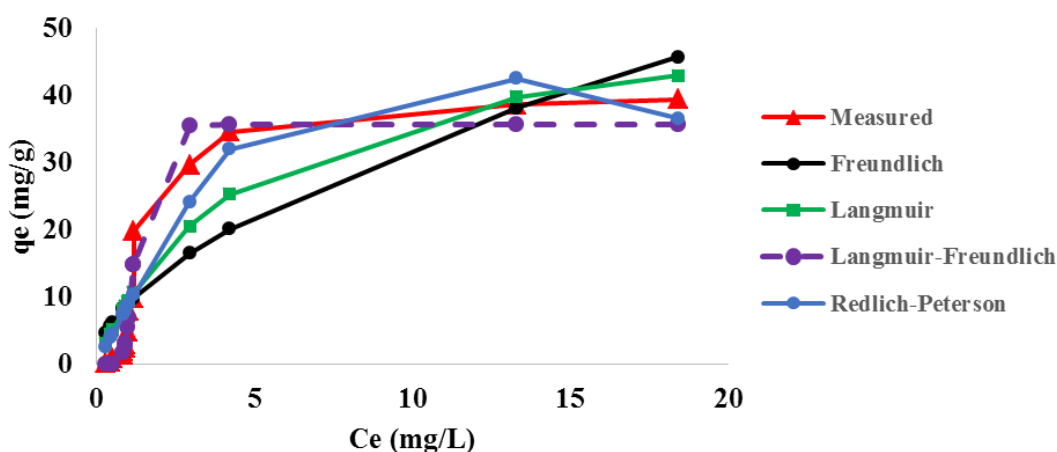**Fig. 10. Caffeine adsorption isotherms by MWCNTs**
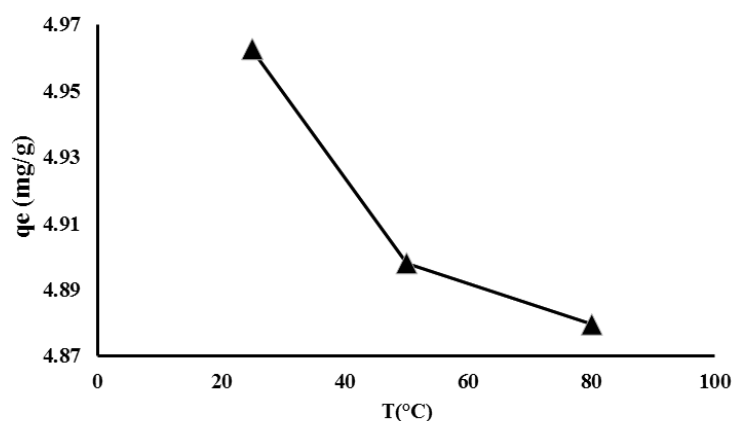
Fig. 11. Impact of temperature on caffeine removal by MWCNTs adsorbent
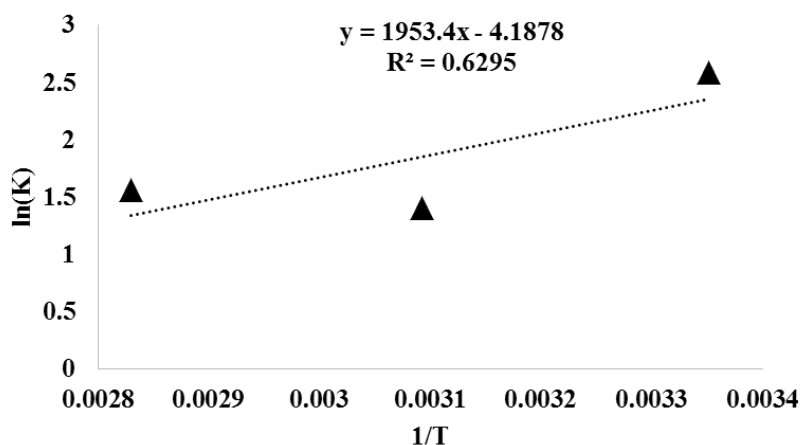

$y = 1953.4x - 4.1878$
$R^2 = 0.6295$

Fig. 12. Plot of ln(K) vs. 1/T for the adsorption of caffeine by MWCNTs

Table 5. Thermodynamic parameters for caffeine adsorption by MWCNTs

	ΔH (KJ/mol)	ΔS (J/mol K)	T(K)	$\Delta G°$ (KJ/mol)
Adsorbent			298	26.63
	16.2	-34.8	323	12.3
			353	11.25

Figure 12 shows the plot of ln(K) vs. 1/T for the adsorption of caffeine on MWCNTs at pH= 7. In order to better understand the impact of raised temperature on the adsorption of the caffeine onto the active sites of the MWCNTs, three basic thermodynamic parameters were studied: the Gibbs free energy of adsorption ($\Delta G°$), the enthalpy change ($\Delta H°$), and the entropy change ($\Delta S°$). Table 5 presents the corresponding values of thermodynamic parameters, showing that ΔH and ΔG are positive for all experiments, while ΔS is negative in most systems. Positive value of ΔG for caffeine indicated that the adsorption process was non-spontaneous. Having calculated the ΔH, the value turned out to be 16.20. This positive value indicated the endothermic adsorption process. Nonetheless, the value of ΔS turned out to be

-34.8, demonstrating that the irregularities lessened by raising the temperature joint solid and liquid phase during adsorption process.

CONCLUSIONS

This study investigated the adsorption of caffeine in aqueous solutions, using MWCNTs under different variables such as pH, the reaction time, the adsorbent dosage, and the initial caffeine concentration. Removal of caffeine was optimal at pH=7 with the equilibrium time being 5 minutes in batch experiments. Higher initial caffeine concentration led to lower removal percentages, but higher adsorption capacity. As the adsorbent dose increased, caffeine removal grew, while the adsorption capacity declined. The caffeine adsorption data was fitted to the Langmuir-Freundlich model, thus, indicating the homogeneity of MWCNTs surface because $1/n >> 1$. The pseudo second-order kinetic model accurately described the adsorption kinetics. Kinetics and thermodynamics results indicated that caffeine adsorption of MWCNTs was a spontaneous and physical process. In general, results addressed the inter-relationships between surface properties of the MWCNTs, chemical structures of the caffeine, and important consequential effects on the adsorption process.

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