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Adsorptive removal of antipsychotic drug by carbon nanofibers in a batch and fixed bed column system

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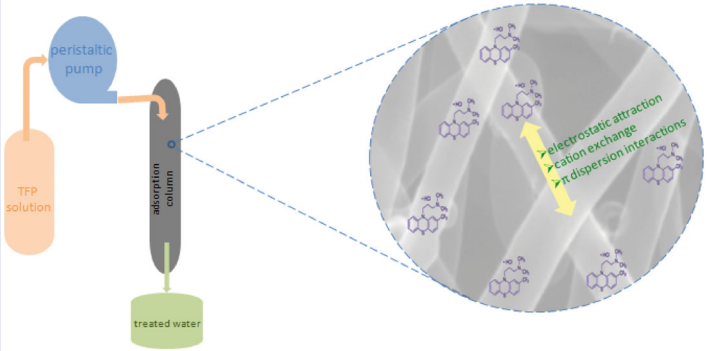
ABSTRACT

Carbon nanofibers are promising green materials for sustainable technology within a wide range of applications including environment, energy, health and high-technology. Accordingly, drug adsorption is an important subject in connection with its environmental and pharmaceutical applications. This study aims to investigate the adsorption performance of carbon nanofibers in batch and fixed bed column processes. Carbon nanofibers were used as adsorbent to remove triflupromazine hdyrochloride from aqueous solutions. Adsorption kinetics were studied using Lagergren first order and Pseudo second order models. Intraparticle diffusion graph was plotted using kinetic data and showed that intraparticle diffusion is the single step controlling the adsorption rate. Experimental equilibrium data was modeled by using Langmuir and Freundlich equations and has a better fit to the Langmuir model. Triflupromazine adsorption on carbon nanofibers was found to be H-type according to Giles classification. The effect of temperature and the effect of pH on adsorption were studied to determine optimum adsorption conditions. Adsorption capacity of carbon nanofibers was decreased with increasing temperature due to the exothermic and physical nature of the process. Thermodynamic parameters confirmed the exothermic nature of the adsorption. Results showed the effective adsorption of drug molecules by carbon nanofibers. Maximum adsorption capacity was calculated as 165.41 mg/g at pH 9 using Langmuir equation. Modeling of the fixed bed column data was done by using Thomas model and Yoon–Nelson model. Results showed the important effect of the operating conditions on the removal performance of carbon nanofibers. Removal capacity was increased with an increase in the flow rate and the increase in the fixed bed length.

KEYWORDS

Carbon nanofibers; adsorption; triflupromazine; nanomaterials; water treatment

GRAPHICAL ABSTRACT



1. Introduction

The presence of pharmaceutically active compounds in water sources are well known based on the results of the recent studies (Fontes et al. 2020; Nassour et al. 2020; Chernova et al. 2021; Gwenzi et al. 2021; Queirós et al. 2021; Schwartz et al. 2021). The discharge of those emerging contaminants has been continued for years and their presence is increasing worldwide as a result of insufficient removal in traditional waste water treatment plants (Karimi-Maleh, Ayati, Davoodi, et al. 2021; Karimi-Maleh, Ayati, Ghanbari, et al. 2021; Karimi-Maleh, Ranjbari, et al. 2021). Traditional waste water treatment plants are not suitable for the removal of drugs from waters (Karimi-Maleh et al. 2020). Waste waters containing these active subtances need to be treated with a second process such as adsorption (Nannou et al. 2020; Yadav et al. 2021).

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Psychiatric pharmaceuticals are a subgroup of pharmaceutically active compounds which are used to treat mental disorders. Several studies reported the detection of the presence of these active chemicals in the aquatic environment in various countries at concentrations of ng/L to µg/L which could effect living organisms importantly (Silva et al. 2015; Anastopoulos et al. 2020; Castillo-Zacarías et al. 2021). Since it is important to remove these active chemicals from waste waters, in this study triflupromazine hydrochloride was selected as a model drug to investigate the adsorption characteristics with carbon nanofibers. Triflupromazine hydrochloride is an important phenothiazine class antipsychotic drug with cationic amphiphilic characteristics. Drug repurposing studies done in the past few months showed that this class of agents has also antiviral activity and the potential utility of phenothiazines in the treatment of Covid-19 based on in vitro studies (Dyall et al. 2014; Ghosh et al. 2020; Hazafa et al. 2020; Pillaiyar et al. 2020; Han et al. 2021; Hashimoto 2021; Machado-Vieira et al. 2021; Xu et al. 2021). Phenothiazine class drugs are also important for having the property to form small aggregates in aqueous solutions (Banipal et al. 2016).

Adsorption using solid adsorbents is the most efficient and economical method to overcome the contamination of natural waters by pharmaceuticals and other pollutants (Çalı şkan Salihi et al. 2016; Yu et al. 2021). Various materials were used as solid adsorbents for the removal of pharmaceuticals from waters (Ahmed and Hameed 2018; Costa and Féris 2020; Hubetska et al. 2020; Qureshi et al. 2020; Rocha et al. 2020; Santamaría et al. 2020; Cheng et al. 2021; Huang et al. 2021; Karimi-Maleh, Ayati, Davoodi, et al. 2021). Kebede et al. have studied the adsorption of antiretroviral and related drugs from waste waters using nanofibrous adsorbent made of Mondiawhitei plant native to the African continent (Kebede et al. 2020). Gupta et al. have used carbon nanofibers synthesized with a microwave-assisted hydrothermal method for the removal of methamphetamine from aqueous solutions (Gupta et al. 2016). Talreja et al. have reported salicylic acid adsorption on carbon bead-supported ethylene diamine-functionalized carbon nanofibers (Talreja et al. 2016). Chaba and Nomngongo have prepared V_2O_5-ZnO coated carbon nanofibers for the removal of cinoxacin and ciprofloxacin (Chaba and Nomngongo 2018), and ZnO coated carbon nanofibers for amoxicillin adsorption (Chaba and Nomngongo 2019). Soberman et al. have studied the adsorption of micropollutants with nanofiber membranes (Soberman et al. 2020). As well as there are few studies on adsorption using carbon nanofibers, there was no study on the adsorption of triflupromazine hydrochloride using carbon nanofibers. Adsorption of triflupromazine hydrochloride on bentonite from waters and in the presence of surfactants was studied in one of our previous studies (Çalı şkan Salihi and Mahramanlı oğlu 2014). Adsorption capacity of triflupromazine hydrochloride was calculated using Langmuir isotherm and compared with four other drugs selected as model molecules. Maximum adsorption capacities were also compared for the adsorption of drugs in the presence of surfactants. Results showed the important effect of amphiphilic molecules present in the medium during the adsorption of drugs. It was also reported in this study that triflupromazine hydrochloride uptake mechanism of bentonite was cation exchange dominantly.

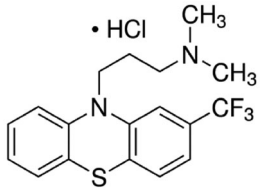

Figure 1. Molecular structure of TFP (Triflupromazine hydrochloride).

Table 1. Properties of triflupromazine hydrochloride (TFP).

Molecular formula	$C_{18}H_{19}F_3N_2S \cdot HCl$
Molecular weight (g/mol)	388.88
Water solubility at 25 °C	Soluble
pK_a at 25 °C	9.2
λ_{max} (nm)	306

The aim of the present study is to investigate the adsorption of triflupromazine hydrochloride from waters using carbon nanofibers. Carbon nanofibers are sp^2-based linear filaments with a nanosize diameter. The parallel fibers always display a hollow core and ordering of atoms within a graphene layer. Fiber form materials are important in scientific and technological applications due to their flexibility, high mechanical superstrength and surface area within a wide range of drug delivery materials to aerospace applications. Carbon nanofibers have the potential to be the primary material of green chemistry and possible green materials technology of the future (De Jong and Geus 2000; Vajtai 2013). Carbon nanofibers have conductive and porous structure promising for several innovations for daily life and high technology products in electronics, environment, energy and catalysis applications (Hammel et al. 2004; Yan et al. 2019).

In the present study, carbon nanofibers were used for the removal of triflupromazine hydrochloride from aqueous solutions. Adsorption kinetics were investigated using two models, i.e., Lagergren first order model and Pseudo second order model. Intraparticle diffusion graph was also plotted and discussed to understand the mechanism of adsorption. Equilibrium studies were done and results were applied to the Langmuir and the Freundlich isotherm models. The Giles adsorption isotherm was used to discuss the affinity between drug molecules and the surface of carbon nanofibers. The effect of temperature and the effect of pH was examined by repeating the adsorption experiments at different temperatures and in drug solutions with various pHs. Fixed bed column data was modeled by using Thomas model and Yoon–Nelson model.

2. Materials and methods

Triflupromazine hydrochloride (TFP) is a phenothiazine class antipsychotic drug and was supplied by Sigma-Aldrich (purity > 98%). TFP was used as received without further purification. Molecular structure of TFP is given in Figure 1 and physicochemical properties of TFP are given in Table 1. Conical shaped carbon nanofibers (CNF) were supplied by

Table 2. Physicochemical properties of carbon nanofibers (CNF).

Density (g/mL)	1.4–1.6
Specific surface area (m^2/g)	54
Pore volume (mL/g)	0.120
Average pore radius (nm)	8.930
pH_{PZC}	4.9

Sigma (>98% carbon basis) and their physicochemical properties were given in Table 2. CNF was washed with DI water prior to use in order to avoid water soluble impurities. The washing was done with 1 L of DI water for per 10 g of CNF using magnetic stirrer. CNF was dried after the washing at 100 °C during 24 hours.

2.1. Characterization of CNF

Scanning electron microscope (SEM-EDX) and X-ray diffraction analysis (XRD) were used to characterize the structure and the morphology of CNF. Other physicochemical properties of CNF were given in Table 2. Surface characteristics of CNF were measured via gas adsorption. PH_{PZC} value was found using mass titration method.

2.2. Batch adsorption studies

Light-tight glass erlenmeyer flasks (100 mL) with caps were used for all the adsorption experiments. Temperature controlled shaker with a water bath was used for shaking the flasks. Samples were collected during and after adsorption and UV absorbances of samples were measured with a spectrophotometer (UV-Visible) at 306 nm. Concentrations of the samples were calculated with the use of standart curves prepared previously. All the experiments were repeated at least three times. All solutions were freshly prepared and used. Preliminary studies were done to determine optimum adsorbent/adsorbate ratio and this ratio was used for all adsorption experiments. The effect of shaking time on the adsorption was studied using 0.01 g CNF and 25 mL of TFP solution at the concentration of 50 mg/L in order to find the time to reach equilibrium. Samples taken at known time intervals were filtered and absorbances were measured using UV-Visible spectrophotometer. Adsorption kinetics were examined using Lagergren 1. order and Pseudo 2. order rate equations. Equilibrium studies were done using 0.01 g CNF and 25 mL of TFP solutions at the concentrations between 5 and 50 mg/L in order to prepare adsorption isotherms. Equilibrium experiments were carried out during equilibrium time in a temperature regulated shaker with water bath. Samples were taken at equilibrium time, then filtered and absorbances of the samples were measured using UV-Visible spectrophotometer. Concentration of all the samples were calculated using calibration curves prepared previously. Giles, Langmuir and Freundlich adsorption isotherms were plotted with equilibrium data and isotherm constants were calculated. The effect of temperature on the adsorption process was examined at the temperatures between 18 °C and 45 °C using the same arrangement given above. The effect of pH on adsorption was also studied at pHs between 1.5 and 9 by repeating the same experimental arrangement. The quantity of adsorption (q, mg/g) was calculated using the following Equation (1):

$$q = \frac{(C_0 - C)V}{w}. \quad (1)$$

C_0 (mg/L) is the initial concentration of TFP solution, C (mg/L) is the concentration of TFP solutions after adsorption, V is the volume of TFP solution (25 mL = 0.025 L) and w is the amount of CNF which is 0.01 g.

2.3. Column studies

Fixed bed column experiments were conducted using borosilicate glass columns and 0.5 g CNF. TFP solutions at a concentration of 100 mg/L were pumped to the column with a flow rate controlled peristaltic pump. The experiments were done by using CNF beds at various lengths between 3 and 7 cm at 25 °C . The effect of flow rate (between 3 and 7 mL/min) was also investigated to determine the effect of operating conditions. The breakthrough curves were prepared using the continuous measurement of effluent concentrations with a UV spectrophotometer. Column data were modeled using Thomas model (2) and Yoon–Nelson model (3).

$$\ln\left(\frac{C_0}{C} - 1\right) = \frac{k_{Th} q_{Th} m}{Q_f} - k_{Th} C_0 t, \quad (2)$$

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

$$q_{YN} = \frac{C_0 \ \tau \ Q_f}{m}. \quad (4)$$

C_0: initial concentration (mg/L); C: effluent concentration (mg/L); k_{Th} and q_{Th}: Thomas model constants; m: mass of adsorbent (g); t: time (min); k_{YN} and τ: Yoon–Nelson model constants; q_{YN}: adsorbate quantity that went through the column (mg/g).

3. Results and discussion

In this study, adsorption of TFP on CNF from aqueous solutions was investigated spectrophotometrically and experimental results were discussed. Physicochemical properties of CNF was given in Table 2. Density of fibers is between 1.4 and 1.6 g/mL in average. Specific surface area was measured using N_2 gas isotherm and calculated as 54 m^2/g. Pore volume and average pore radius are 0.120 mL/g and 8.930 nm, respectively. CNF is a porous material with pores at nanometer scale. Dimensions, shape and surface morphology of CNF were scanned with SEM (Scanning Electron Microscope) and SEM photos were given in Figure 2. Fibers at nanoscale are clearly seen in the both SEM images. Dimension of the fibers are about 100 nm × 20–200 μm in average. EDX (Energy-dispersive X-ray) analysis is a common method used by materials science researchers in order to have information about chemical composition of the materials. It gives information on the elements present in

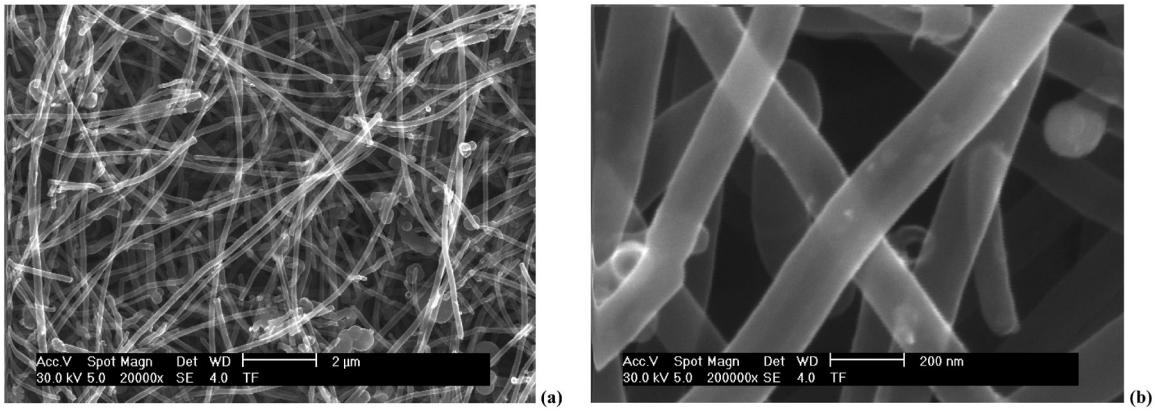

Figure 2. SEM images of CNF.

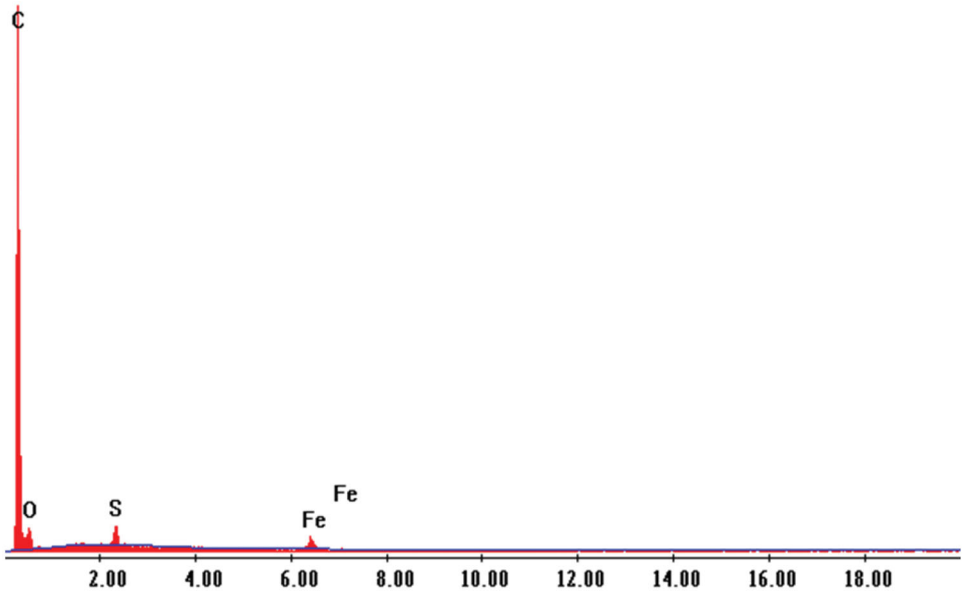

Figure 3. EDX analysis of CNF.

the structure. EDX analysis was done to analyze elemental composition of CNF and given in Figure 3. EDX analysis confirmed the carbon structure of CNF.

XRD analysis is a nondestructive test method and used for phase identification, so to reveal the composition of the materials. XRD analysis of CNF was done in order to further confirm the structure of CNF and XRD spectrum was given in Figure 4. Recorded XRD spectrum where CNF shows two peaks is in accordance with the previous studies. The peak at around 2θ of 25 is a strong reflection which can be assigned to the (002) plane indicating the amorphous nature of carbon. Interlayer distance (d_{002}) was calculated as 0.33 nm for CNF using the equation of Bragg's law (5); where n is the order of reflection, λ is the wavelength of the rays, d is the interlayer distance and θ is the angle between the incident rays and the surface of the crystal. The weak reflection peak at around 2θ of 45 is corresponding to (100) planes of the graphite structure (Lai and Lo 2015; Nie et al. 2019).

$$n\lambda = 2d \sin\theta. \quad (5)$$

Adsorption studies were done using CNF without any pretreatment except washing and drying. TFP adsorption on CNF was studied at 25 °C using 25 mL TFP solutions and 0.01 g CNF. The effect of time on the adsorption was studied to find the equilibrium time of the adsorption. Time to reach equilibrium was found to be 30 min using TFP solutions at the initial concentration of 50 mg/L (Figure 5). TFP adsorption on CNF is advantageous because it is a fast process and adsorption process achieves the equilibrium in a short time like 30 min. Equilibrium time states the duration when the adsorption of molecules finishes practically.

Kinetic experiments were done by taking samples at known time intervals. Then the concentrations of the samples were measured. Adsorption quantity (q) at specific times were calculated using the concentrations measured. Kinetics of TFP adsorption on CNF were modeled by using Lagergren first order (Figure 6) and Pseudo second order (Figure 7) equations. Kinetic parameters were calculated and given in Table 3. As can be seen from Table 3, TFP adsorption on CNF gave the best fit to the Lagergren first order model (6) according to the comparison of correlation coefficients (R^2). However, it also has a good fit to the Pseudo second order model (7) according to correlation coefficients (R^2) that shows the model fitting. k_1 is the rate constant of

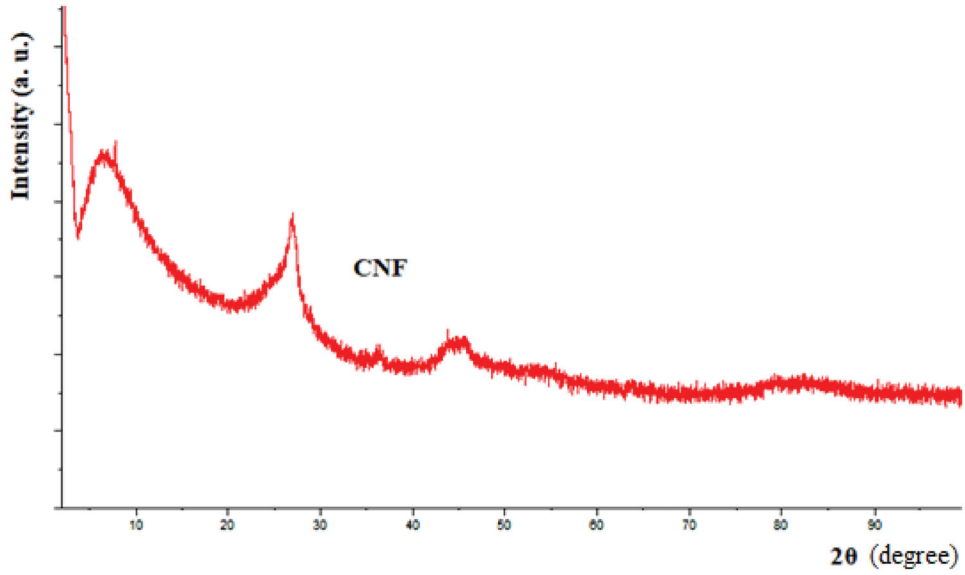

Figure 4. XRD spectra of CNF.

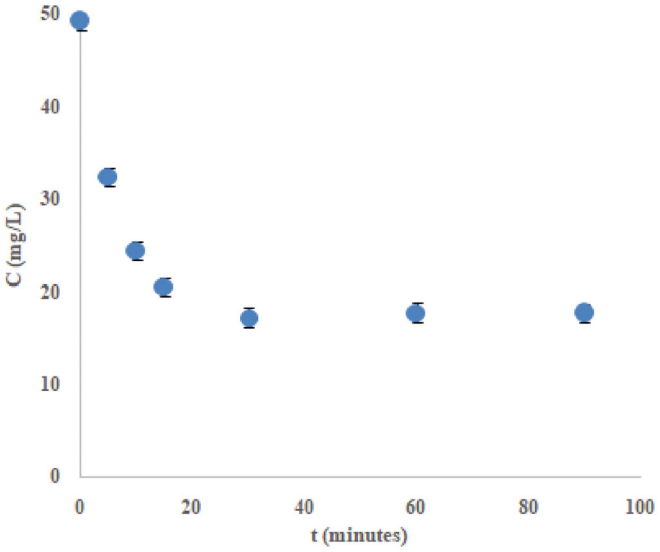

Figure 5. Effect of shaking time on the adsorption of TFP on CNF.

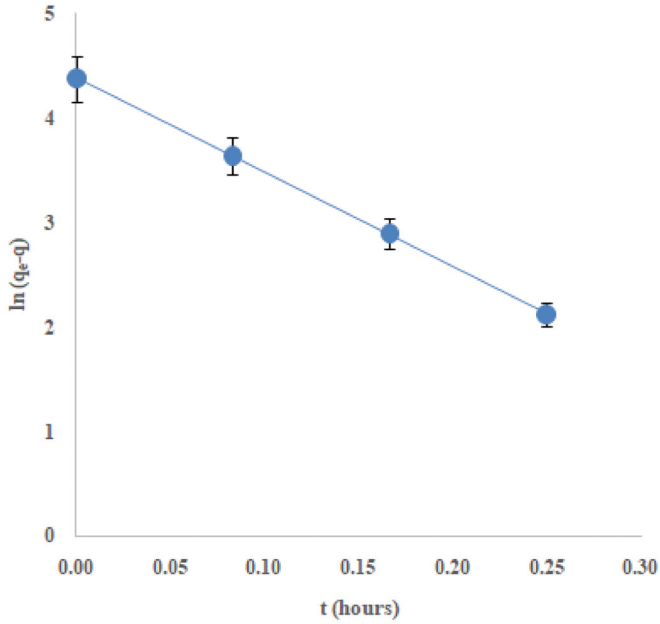

Figure 6. Lagergren first order graph for the adsorption of TFP on CNF.

Lagergren first order model and k_2 is the rate constant of Pseudo second order model. q_e in the equations shows the adsorption quantity (mg/g) at equilibrium and q shows the adsorption quantity (mg/g) at any time.

$$\ln(q_e - q) = lnq_e - k_1 t, \tag{6}$$

$$\frac{t}{q} = \frac{1}{k_2 q^2} + \frac{1}{q_e} t. \tag{7}$$

Intraparticle diffusion graph (Figure 8) was also plotted using the results of the effect of time experiments. Intraparticle diffusion constant (k_D) was calculated as 145.8 mg/g hours^{0,5} using this linear graph. The graph shows the presence of intraparticle diffusion in this process. The linear plot passes from the origin and demonstrates intraparticle diffusion which controls the rate of this adsorption process solely (Çalışkan and Göktürk 2010; Çalışkan Salihi et al. 2021). The equation for the intraparticle diffusion was given below.

$$q = k_D t^{0.5}. \tag{8}$$

Equilibrium studies were done after determining the time to reach equilibrium. Experiments of TFP adsorption on CNF were conducted at the concentration range between 5 and 50 mg/L using 0.01 g CNF during 30 min at 25 °C. Giles isotherm (Figure 9) was plotted using the equilibrium data. C (mg/L) and q (mg/g) shows the values of concentration of TFP and adsorption quantity measured and calculated at the equilibrium. TFP adsorption on CNF was H-type according to Giles classification. H-type isotherm is the special type of L-type isotherm and shows the high affinity between adsorbate and the adsorbate. TFP molecules showed high affinity

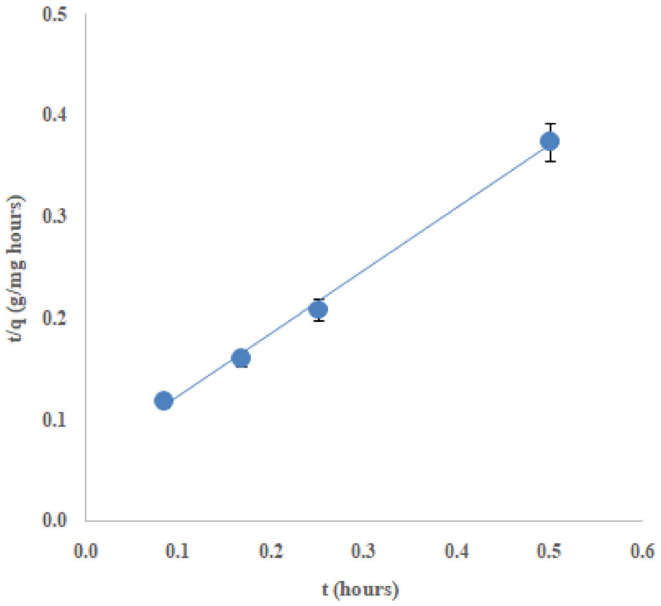

Figure 7. Pseudo second order graph for the adsorption of TFP on CNF.

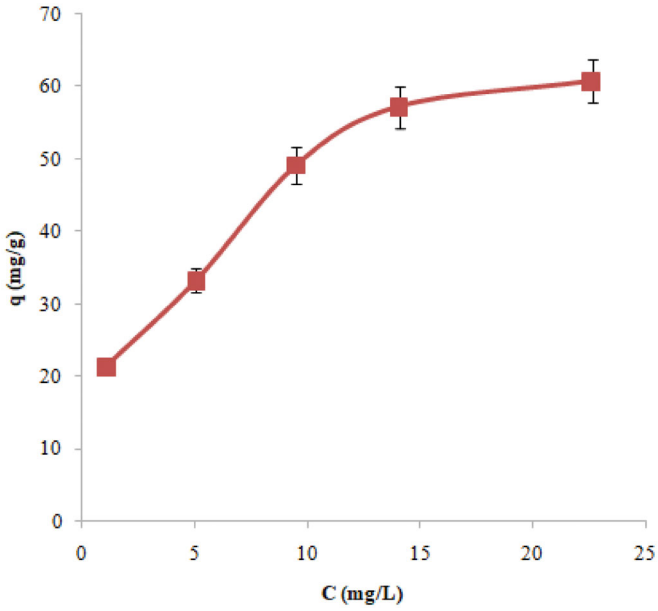

Figure 9. Giles isotherm of the adsorption of TFP on CNF.

Table 3. Kinetic parameters for the adsorption of TFP on CNF.

Lagergren first order model			Pseudo second order model		
k_1 (1/s)	q_1 (mg/g)	R^2	k_2 (g/mg.s)	q_2 (mg/g)	R^2
9.02	78.14	0.999	6.33	1.61	0.997

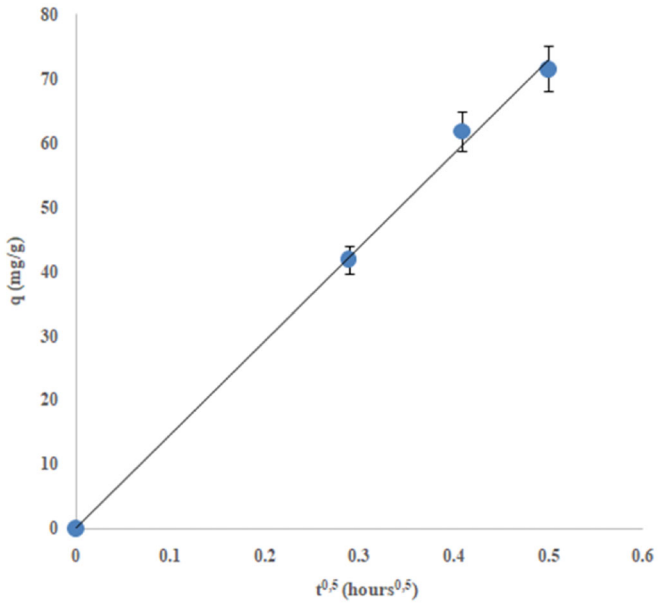

Figure 8. Intraparticle diffusion graph for the adsorption of TFP on CNF ($R^2 = 0.997$).

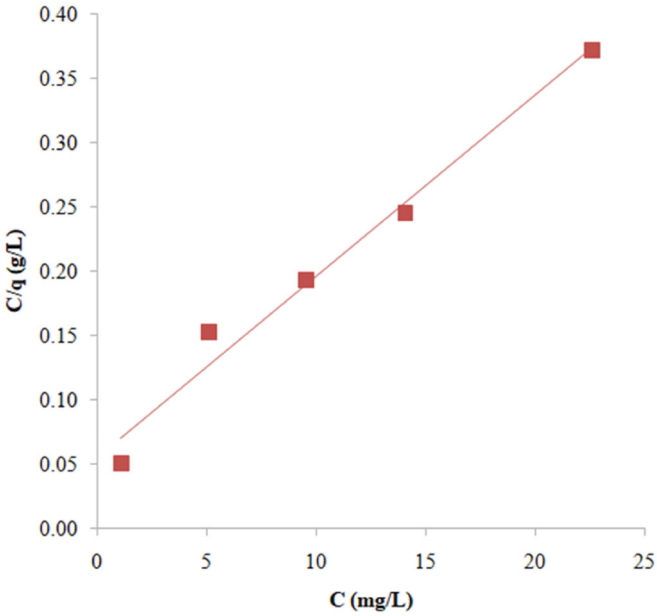

Figure 10. Langmuir isotherm of the adsorption of TFP on CNF.

to the CNF surface (Giles et al. 1960). High affinity means the tendency of TFP molecules to be adsorbed on CNF.

Langmuir (Figure 10) and Freundlich (Figure 11) isotherms were also plotted using the equilibrium data. Isotherm constants were calculated and given in Table 4. The adsorption of TFP on CNF has a better fit to the Langmuir model (9) than the Freundlich model (10) according to R^2 values (Table 4). Q (mg/g) shows the maximum adsorption capacity calculated using Langmuir model. Adsorption phenomena covers nearly all of the surface chemistry and physics, because various adsorption processes have complexity and involves physical and chemical changes in a complicated medium. The molecules tend to orient themselves in definite ways on the surface. Adsorption occurs as a result of forces between the solid surface and particular atoms or atom groups of the molecules to be adsorbed. The Langmuir model shows that it becomes more difficult to find empty adsorption sites for the adsorbate molecules as the adsorption occurs. Adsorbate molecules do not locate vertically and there isn't a strong race between the molecules of the adsorbate, i.e., TFP and the solvent, i.e., water (Langmuir 1918). Adsorption capacity was calculated

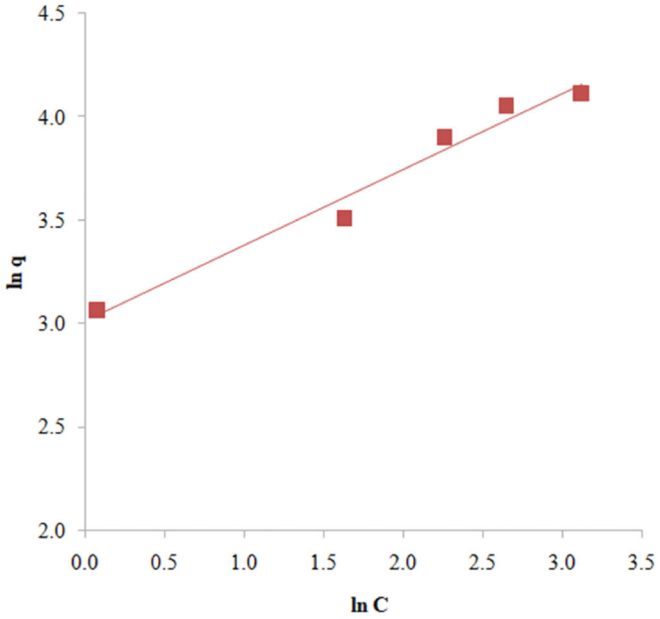

Figure 11. Freundlich isotherm of the adsorption of TFP on CNF.

Table 4. Isotherm parameters of the adsorption of TFP on CNF.

Langmuir model			Freundlich MODEL		
Q (mg/g)	b (L/g)	R^2	k	n	R^2
71.43	0.25	0.997	19.86	0.37	0.972

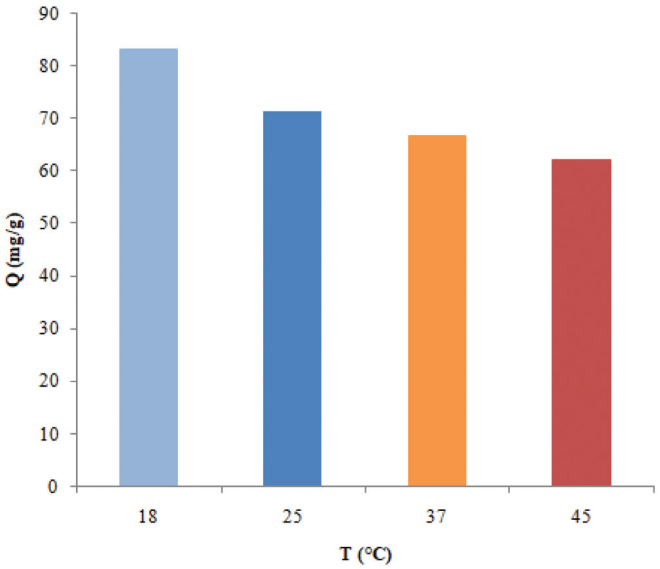

Figure 12. Effect of temperature on the adsorption of TFP on CNF.

using the Langmuir equation and showed that CNF can be used as an adsorbent with high capacity for the adsorption of TFP effectively.

$$\frac{C}{q} = \frac{1}{Qb} + \frac{C}{Q}, \tag{9}$$

$$lnq = lnk + n\ lnC. \tag{10}$$

Temperature is an important parameter to see the effect of seasonal changes on the removal of contaminants by adsorption. The effect of temperature on the adsorption of

Table 5. Thermodynamic parameters for the adsorption of TFP on CNF.

		ΔG (J/mol)			
ΔH (J/mol)	ΔS (J/mol K)	18 °C	25 °C	37 °C	45 °C
−4,548.86	−13.86	−441.13	−472.30	−382.55	−26.31

TFP on CNF was studied between 18 °C and 45 °C and summarized in Figure 12. Results show the significant effect of temperature on TFP adsorption by CNF and the highest adsorption capacity was achieved at 18 °C. Adsorption capacities were calculated using Langmuir isotherm. Adsorption capacity of TFP on CNF decreased with the increase in the temperature. This decrease observed in the capacity shows the exothermic and physical nature of the adsorption. The increase in the temperature has weakened the attractive forces between TFP molecules and CNF surface (Çalışkan Salihi and Mahramanlı oğlu 2014). Attractive forces takes place between TFP and CNF surface were discussed below. Thermodynamic parameters were also calculated for the adsorption of TFP on CNF using the Van't Hoff Equation (11) and given in Table 5.

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{11}$$

Values of ΔH and ΔS were computed from the slopes and intercepts of linear variations of lnK with the reciprocal of temperature. Negative value of the enthalpy change (ΔH) confirmed the exothermic and physical nature of the adsorption. Physisorption and chemisorption can be classified by the size of the enthalpy change. The processes with an enthalpy change of <84 kJ/mol can be accepted as physical adsorption. The negative values of the entropy of adsorption (ΔS) shows the decreased randomness between the CNF surface and TFP solution. The free energy of adsorption (ΔG) was calculated from the following equation:

$$\Delta G = -RT \ln K \tag{12}$$

where K is the distribution constant and T is the temperature (K); R is the gas constant (8.314 J/mol K). Negative ΔG values indicate the feasibility and spontaneity of the adsorption process (Pouya et al. 2015). However this spontaneity decreases with an increase in temperature. Similar results were found in our previous studies for the adsorption of drugs on activated carbon (Çalışkan and Göktürk 2010).

The effect of the pH of the environment was studied between pHs 1.5–9. The results were summarized in Figure 13. Adsorption quantity of TFP on CNF decreased with an increase in the pH at the pH values lower than 3.5. However, there is an increase in the adsorption quantity at the pH values higher than 5.5 due to the changes of charges on adsorbent and adsorbate. Maximum capacity for the adsorption was found at pH 9. The reason of the important increase in the adsorption quantity at the alkaline pHs is the electrostatic attraction forces between cationic TFP molecules and negatively charged CNF surface, because CNF surface is negatively charged at the pHs higher than its pH_{PZC} which is 4.9. However, adsorption capacity increases with the increase of acidity at the pHs lower than 4.9. This

increase shows the cation exchange which becomes favorable due to the increase of the positive charges on the CNF surface. Because CNF surface is charged positively at the pHs lower than its pH_{PZC} (4.9). Adsorption still occurs at the pHs around pH_{PZC} (around the pH point of zero charge) showing dipole and π-π dispersion interactions are also effective besides cation exchange (Tulay 2020). π-π interactions are dominant supramolecular forces in carbon structures like fullerenes, graphene, carbon nanotubes and nanofibers. The group of dispersion interactions govern the supramolecular chemistry of carbon based materials and usually characterized as having strong geometric requirements (Hunter and Sanders 1990; Pérez and Martín 2015; Zhou 2015). Our previous studies also shows the importance of π dispersion interactions in the adsorption of drug molecules (Çalışkan Salihi 2017; Çalışkan Salihi and Aydın 2017; Çalışkan Salihi et al. 2019).

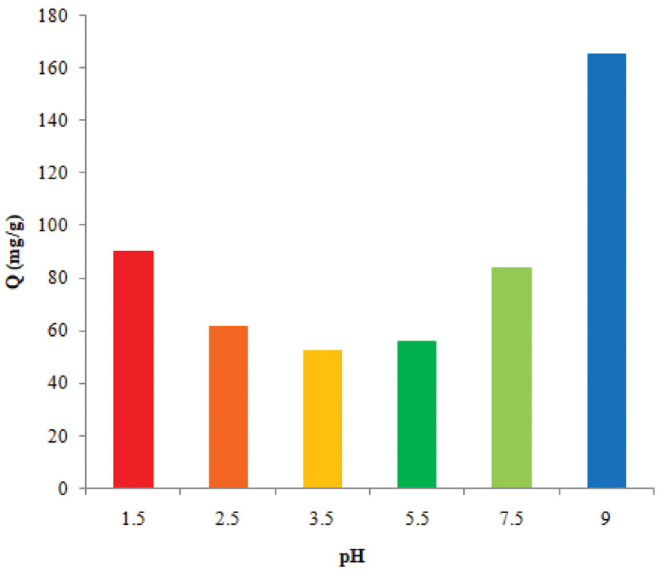

Figure 13. Effect of pH on the adsorption of TFP on CNF.

Column studies were conducted using various experimental conditions in order to determine the effect of column operating conditions. Fixed bed adsorption studies were done using 0.5 g of CNF for the adsorption of TFP at an initial concentration of 100 mg/L. Figure 14 shows the effect of flow rate between 3 mL/min to 7 mL/min on the removal performance of TFP. Figure 15 shows the effect of the length of the fixed bed on the removal performance of TFP. Fixed bed column adsorption parameters were given in Table 6. As seen from the table, adsorption becomes more effective with an increase in the flow rate. This fact is in good agreement with the rapid adsorption of TFP on CNF which was disclosed above. Similar results were indicated in the previous studies (Sotelo et al. 2012). The length of fixed bed was also effective on the removal performance of TFP (Figure 15). The increase in the fixed bed length provides a more efficient removal due to increased contact time of TFP solution with the bed. TFP solution could meet more active sites during contact with a longer fixed bed. Similar results were reported about the increased adsorption performance of the fixed bed when the length was increased (Albayati and Kalash 2020). Linear regression analysis which is a statistical method to estimate the relationships between dependent and independent variables was used to determine the model fitting. Models showed a good fitting to the experimental data according to R^2 values (Table 6). Calculated adsorption capacities showed the important effect of the operating conditions on the removal efficiency (de Franco et al. 2018) of TFP on CNF bed.

This study showed that CNF can be used as an effective adsorbent for the removal of TFP from waters. In the current literature, there was no study on the adsorption of TFP using carbon based adsorbents. There is only one study on the adsorption of TFP which is one of our previous studies and focus on the removal of five drugs including TFP using

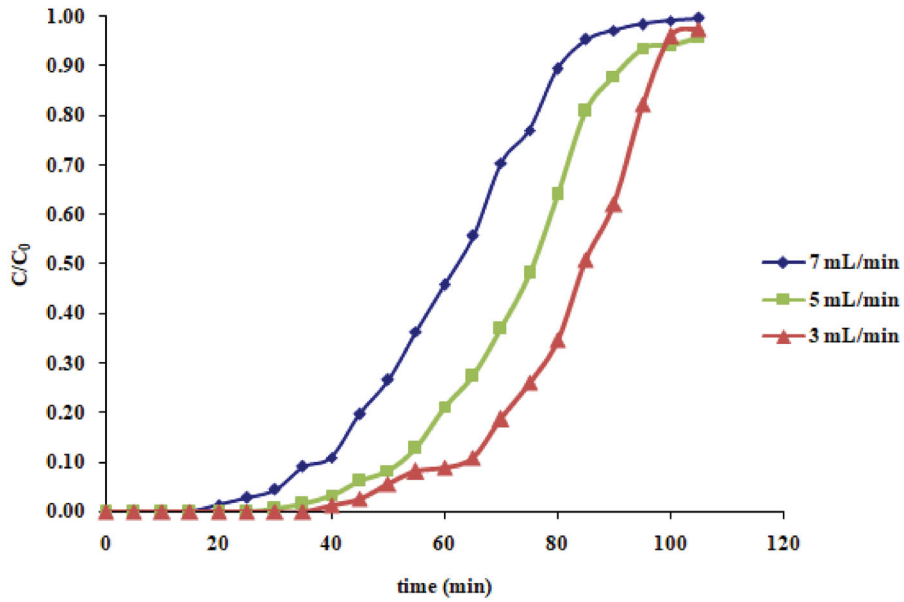

Figure 14. Effect of flow rate on the removal performance of TFP.

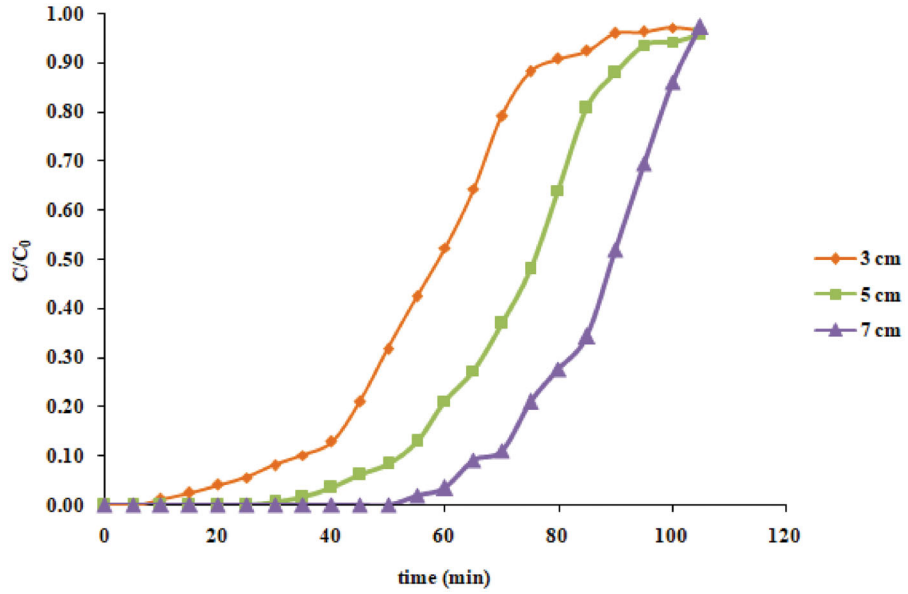

Figure 15. Effect of the length of the fixed bed on the removal performance of TFP.

Table 6. Fixed bed column adsorption parameters for TFP adsorption on CNF.

Experimental conditions			Batch adsorption (Langmuir model)	Thomas model			Yoon–Nelson model			
L (cm)	Q_f (mL/min)	C_0 (mg/L)	q_{exp} (mg/g)	q_{Th} (mg/g)	k_{Th} (ml/mg.min)	R^2	q_{Yn} (mg/g)	k_{Yn} (min^{-1})	T (min)	R^2
3	5	100	71.43	56.14	0.8013	0.945	56.14	0.081	55.54	0.945
5	7	100		83.40	1.1080	0.989	83.40	0.112	58.94	0.989
5	5	100		74.66	1.0586	0.986	74.66	0.107	73.86	0.986
5	3	100		48.50	1.1080	0.949	48.50	0.112	79.96	0.949
7	5	100		86.61	1.3059	0.958	86.61	0.132	85.68	0.958

bentonite (Çalışkan Salihi and Mahramanlıoğlu 2014). CNF is a carbon based adsorbent with a highly hydrophobic surface. Interlayer distance for CNF was calculated as 0.33 nm using XRD data as indicated above. TFP has hydrophilic character and it is a relatively big molecule to penetrate into interlayer distance. The results of the kinetic calculations also showed that intraparticle diffusion step is the rate controlling step in this process. It came out that TFP physisorption occurs mainly on the outer surface of CNF. Adsorption capacity for TFP on CNF was found to be 71.43 mg/g in the batch system at 25 °C (Table 4). In the fixed bed column system, adsorption capacities were found between 56.14 mg/g and 86.61 mg/g at various operating conditions. Adsorption capacity was found to be 56.14 mg/g when 3 cm fixed bed column used with a 5 mL/min flow rate. Adsorption capacity was increased to 86.61 mg/g when 7 cm fixed bed column was used with the same flow rate. Longer fixed bed column has the advantage ensuring an increased contact time for CNF and TFP. It is also important that TFP adsorption on CNF is a fast process with an equilibrium time of 30 min for the effective removal of TFP using fixed bed column system (Sotelo et al. 2012; de Franco et al. 2018; Albayati and Kalash 2020).

4. Conclusion

The removal of an antipsychotic drug triflupromazine was evaluated in this study using batch and fixed bed column adsorption methods. CNF with a surface area of 54 m^2/g was used as a nanoscale adsorbent in this study. The results of the present study showed that CNF is an efficient adsorbent for the removal of TFP from waters. Being fast is an advantage of CNF adsorption. Equilibrium time for the adsorption is 30 min. Adsorption kinetics were modeled using Lagergren first order and Pseudo second order equations. Both models fitted to the experimental data, but the Lagergren first order model gave a better fit. Intraparticle diffusion graph was plotted and showed that intraparticle diffusion step is the only step that controls the rate of adsorption. H-type Giles isotherm showed the high affinity between TFP molecules and CNF surface. Equilibrium data has a better fit to the Langmuir model than the Freundlich model. Adsorption capacities were calculated using Langmuir equation and adsorption capacity was decreased when the temperature was increased. Temperature has an important effect on adsorption and TFP adsorption on CNF is physical and exothermic in nature. pH of the environment also has an important effect on adsorption. Maximum adsorption capacity was found to be 165.41 mg/g at pH 9. This work is important for the removal of drug toxicity from the environment and column experiments showed the improved performance achieved by adjusting the operating conditions. Column studies were done using several experimental conditions. Adsorption capacity of CNF has increased with an increase in the flow rate of TFP solution and the length of the fixed bed.

Disclosure statement

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