Desalination and Water Treatment
www.deswater.com
doi: 10.5004/dwt.2020.26312

206 (2020) 331–339
December

Adsorption characteristics of diclofenac sodium onto graphene nanoplatelets

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Received 2 May 2020; Accepted 4 July 2020

ABSTRACT

Adsorption characteristics of diclofenac sodium (DCS) onto graphene nanoplatelets (GNP) were evaluated in this study. Batch adsorption experiments were carried out to study the efficiency of GNP to remove DCS. Optimum conditions such as contact time, adsorbent dosage, the initial concentration of DCS, pH, and temperature were investigated for the maximum removal of DCS. Maximum removal of 99% was observed at 25°C temperature, 3.5 g/L dosage of GNP, pH of 5, 5 mg/L concentration of DCS, and a contact time of 40 min. Moreover, three different isotherm models were applied to study the interactions between molecules of adsorbate and adsorbent. Langmuir isotherm was found to most suitable fit the data with an R^2 value of 0.9967 and the Langmuir constant (K_L) was found to be 1.0363 L/mg. Kinetic models were also examined, and it was observed that the adsorption process follows pseudo-second-order kinetics with a rate constant K_2 = 1.8218 g/mg min. Finally, thermodynamic properties were calculated using Sip's model which reflected the negative value of change in Gibbs free energy and the change in enthalpy was equal to –3.9089 KJ/mol confirming that the process is exothermic and spontaneous.

Keywords: Pharmaceuticals; Diclofenac sodium; Graphene nanoplatelets; Adsorption

1. Introduction

Worldwide, there is an increase in demand and supply of pharmaceuticals, leading to an increase in wastewater generation from pharmaceutical industries. Pharmaceuticals are compounds used in the cure or prevention of diseases. Waste containing active pharmaceutical ingredients (API) from human and animal excreta, land runoff, hospitals, and R&D facilities is becoming a serious environmental threat [1,2]. A main concern is that water generated from these sources is polluted with biologically persistent chemicals and degradation resistive compounds. Studies on the toxicity of pharmaceutical compounds show that they are hazardous to humans and to other organisms such as aquatic life and birds [3–6]. Moreover, many studies have shown that long term exposure to low concentrations of pharmaceutical compounds has led to drastic effects in aquatic and marine life, such as acute and chronic damages, behavioral changes, changes in sexual orientation of fish, tissue accumulation, decrease in reproductive efficiency, amongst others [1,5,7]. One of the most prescribed and consumed, drugs in the world is diclofenac sodium (DCS) [8]. DCS is a prevalent non-steroidal anti-inflammatory drug (NSAID) and is primarily used in the treatment of pain and inflammations [9]. On the other hand, studies have shown that DCS was the cause of the extinction of vultures in the subcontinent region [6]. Toxic effects of DCS, include damage of renal and gastrointestinal tissue in vertebrates, consequently leading to death [7]. On the other hand, no regulations for DCS in water bodies have been enforced to this day, except for the

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inclusion in the first watch list of the water framework directive of the European Commission to understand its effect in the environment [10]. As a result, special attention needs to be given in order to find efficient removal techniques to minimize its environmental effects.

Researchers have found that the conventional process carried out by wastewater treatment plants (WWTPs) have low efficiency in the removal of DCS during the treatment process (40%–50%) [11]. Due to its high solubility in water (5,000 mg/L) and inefficiency of the removal processes, it is frequently detected in reasonable quantities in treated and untreated wastewater [12,13].

Several techniques have been used to remove pharmaceuticals and personal care products (PPCPs) from wastewater. These include, but are not restricted to, biodegradation, advanced oxidation processes (AOP), ozonation, Fenton–oxidation, photodegradation, and hybrid processes [14]. However, these techniques are restricted in use due to their high operational cost and the production of toxic by-products [15]. An efficient alternative method for the removal of chemicals from wastewater is adsorption. Adsorption is a widely used process applied for many decades in removal of unwanted substances from fluids. The advantages of adsorption over other removal techniques, include the fact that it is economic and straightforward operation. The availability of a variety of adsorbents has made the adsorption-based techniques a beneficial treatment method for the removal of different micro pollutants including pharmaceuticals [16–18]. In addition, adsorption does not generate by-products and the adsorbents can be regenerated and/or recycled, which is an essential and useful aspect of the adsorption process [19].

In general, there is a strong focus in finding new and improved adsorbents to enhance the efficiency of the adsorption technique. A good alternative for adsorbents is the use of graphene. Graphene is a fascinating material that has drawn the attention of scientists due to its unique characteristics that renders it an effective material in different applications ranging from electronics to wastewater treatment [20]. Graphene has been used extensively in the field of wastewater treatment to remove various pollutants such as dyes, emulsified oils, and pharmaceutical compounds [14,20–22].

The aim of the present work was to study the potential use of graphene nanoplatelets (GNP) in the adsorption of DCS by obtaining experimentally the optimum conditions for the maximum removal of DCS. Moreover, the effectiveness of graphene was assessed by studying the effect of different parameters such as contact time, adsorbent dosage, initial pH, the initial concentration of DCS, and temperature. Finally, the adsorption process was studied by fitting the results obtained to the different kinetic and isothermal models and calculating essential thermodynamic parameters.

2. Materials and methods

2.1. Materials

DCS was obtained from local pharmaceutical industry in the U.A.E. and was used without further purification. GNP, 99% pure, were purchased from Grafen Chemical Industries in Turkey. Distilled water was used to prepare all stock solutions. The pH of the solution was adjusted using 0.1 M solutions of HCl and NaOH.

2.2. Instrumentation

Adsorption was carried out in a temperature controlled multi-stack refrigerated shaking incubator (DAIHAN Scientific, South Korea). Orion 201A+ basic pH meter (Thermo Electron Corporation, USA) was used to measure the pH of the solution. The UV-vis measurements were carried out using Cary 50 Conc (Varian, Australia), 0.45 μm MCE syringe filters (Chrome Tech, Germany) were used to filter the solution after adsorption experiments and prior to UV-vis analysis.

2.3. Adsorption experimentation

The stock solution of DCS (200 mg/L) was prepared by dissolving 100 mg of DCS in 500 mL of distilled water. Dilutions of the stock solution at different concentrations were prepared for the adsorption experiments. The solutions were then transferred to 50 mL Erlenmeyer flasks. A known mass of graphene was added each solution and placed in a shaking incubator at a specified temperature for a certain time with fixed shaking speed. The solutions were then filtered using 0.45 μm syringe filters. The absorbance of the solution was measured through UV-vis spectroscopy. The final concentration was calculated using a calibration curve, and removal efficiency was calculated using the Eq. (1) is given as:

$$\text{Removal } \% = \frac{\left(C_o - C_e\right)}{C_o} \times 100 \tag{1}$$

where C_0 and C_e are the concentrations (mg/L) of DCS before and after the adsorption study, respectively.

3. Results and discussion

3.1. Adsorption studies

Different parameters were varied to find out the optimum conditions for the removal of DCS by GNP. The different parameters include contact time (5–120 mins), dosage of GNP (0.5–4.0 g/L), initial pH of the solution (3–11), initial concentration of DCS (5–25 mg/L), and temperature (25°C–45°C). After filtration, the drug content was quantified using UV-vis spectroscopy at a wavelength of 276.1 nm. The effect of each experimental parameter was optimized and discussed in the following sections.

3.1.1. Effect of contact time

The effect of contact time on the removal efficiency is shown in Fig. 1. Inspection of Fig. 1 reveals that the percent removal of DSC by GNP increases with increasing contact time until equilibrium is reached. This behavior indicates that the kinetics of the adsorption process is not fast in nature, indicating that some activated elementary steps are involved in the process. Once enough time is given,

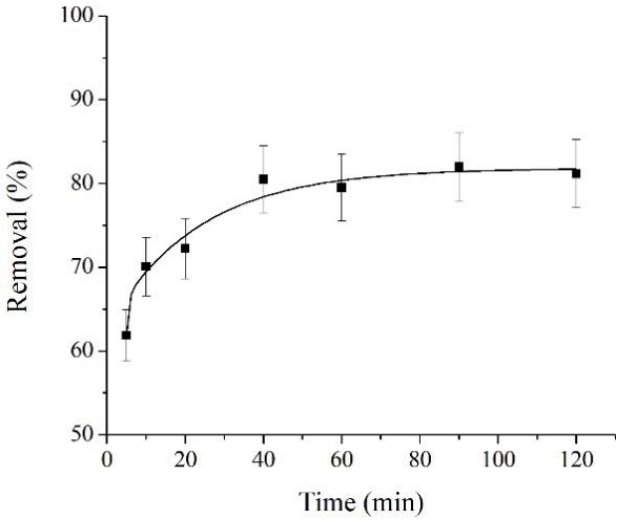

Fig. 1. Effect of contact time on removal efficiency of DCS by GNP. Shaker speed: 150 rpm, initial pH = 7 ± 0.1, temperature = 25°C, GNP dosage = 2 g/L, and initial concentration of DCS = 10 mg/L.

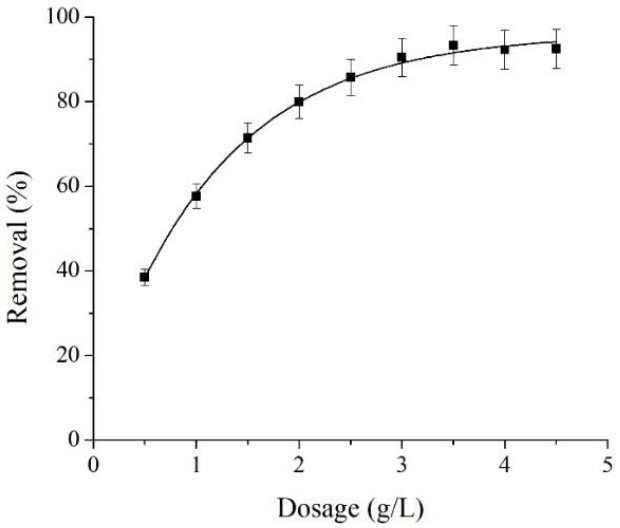

Fig. 2. Effect of GNP dosage on removal efficiency of DCS by GNP. Shaker speed: 150 rpm, contact time = 40 min, initial pH = 7 ± 0.1, temperature = 25°C, and initial concentration of DCS = 10 mg/L.

the rate-determining step is overcome and equilibrium is established. As shown in Fig. 1, the equilibrium time for the removal of DCS is achieved at 40 min. Further details on the adsorption mechanism are discussed in section 3.3 (Adsorption kinetics).

3.1.2. Effect of GNP dosage

Fig. 2 shows the effect of GNP dosage on the removal efficiency of DSC at the optimal contact time. The dosage was varied from 0.5 to 4.5 g/L. The results show that the removal efficiency increases with increasing GNP dosage. This observation could be attributed to the introduction of active sites as a result of increasing the dosage until all DSC is adsorbed and hence is becoming the limiting reactant leading to an observed plateau. Consequently, no further increase was observed after a dosage value of 3.5 g/L indicating that after this dosage all available sites are saturated with DSC leading to diminishing the driving forces for adsorption.

3.1.3. Effect of pH

Initial pH can affect both the speciation of the DSC and the surface charge of GNP. To quantify and understand the effect of pH on the removal efficiency of DSC by GNP, the pH was varied between 2 and 11. It can be observed from Fig. 3a that the removal efficiency remains constant under

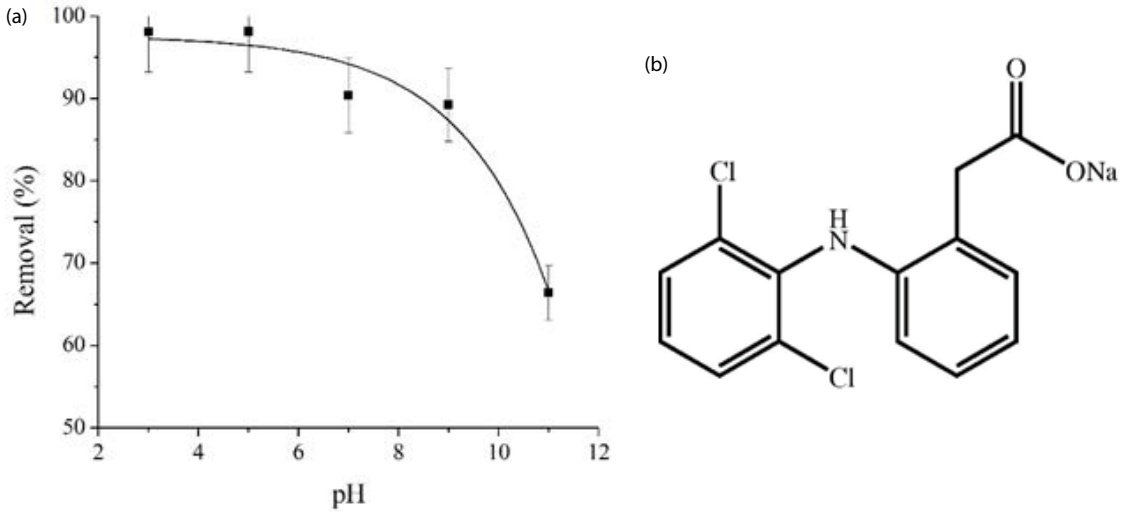

Fig. 3. (a) Effect of initial pH on removal efficiency of DCS by GNP. Shaker speed: 150 rpm, contact time = 40 min, temperature = 25°C, GNP dosage = 3.5 g/L, initial concentration of DCS = 10 mg/L and (b) structure of diclofenac sodium.

acidic conditions (below 5) when the pH is below the pK_a value of DCS (4.2), while it decreases gradually at mild basic conditions and significantly at a strong basic environment (above 9). The maximum removal efficiency was obtained at a pH of 5.0. To provide an understanding of the structural influence of pH on DCS, the structure of DSC is shown in Fig. 3b. It has been observed that electrostatic attractions or repulsions play an important role in defining the interaction of adsorbents with ionizable pollutants [16]. DCS behaves as a neutral molecule under acidic pH conditions, thus showing more attraction to the graphene surface [23]. Furthermore, GNP shows a negative charge on the surface for pH conditions greater than 2.2 [20], hence the hydrophobic effects as well as the π–π electron-donor attractions play a major role in the adsorption process for pH < pK_a of DCS. At pH conditions greater than 4.2, DCS ionizes to give a negatively charged ion that is electrostatically repelled by GNP surface leading the observed decrease in the removal efficiency.

3.1.4. Effect of DCS concentration

The effect of the initial concentration of DCS on the removal efficiency was also studied (Fig. 4) Inspection of this figure reveals that the percent removal of DSC by GNP is gradually decreased with increasing its initial concentration. This observation could be attributed to the fact that at constant GNP dosage, the available sites becomes the limiting factor as the concentration of DSC increases, leading the observed saturation.

3.1.5. Effect of temperature

After selecting the optimal parameters for pH, adsorbent dosage, contact time, and initial concentration of DCS. The effect of temperature on the percent removal of DSC by GBP was studied (Fig. 5). Inspection of Fig. 5 reveals that the percent removal is slightly decreased with increasing temperature, reaching a value of 95% at 45°C. The slight decrease in the percent removal indicates that the adsorption process is exothermic in nature. According to the obtained results, the optimum temperature was 25°C.

3.2. Adsorption isotherms

To obtain a better understanding of the adsorption process and an insight of the interactions between adsorbent and adsorbate, adsorption isotherms were plotted for the different models. Optimum conditions were used to obtain the adsorption isotherms From the previous experiments, the following optimal conditions were used: Temperature of 25°C, contact time of 40 min, initial pH of 5, GNP dosage of 3.5 g/L, and initial concentration of DCS of 5 mg/L. In these experiments, the equilibrium adsorption capacity (Q_e) was calculated at several equilibrium concentrations of DSC using Eq. (2). The obtained data were fitted different isotherm models.

$$Q_e = \frac{\left(C_o - C_e\right)V}{m} \quad (2)$$

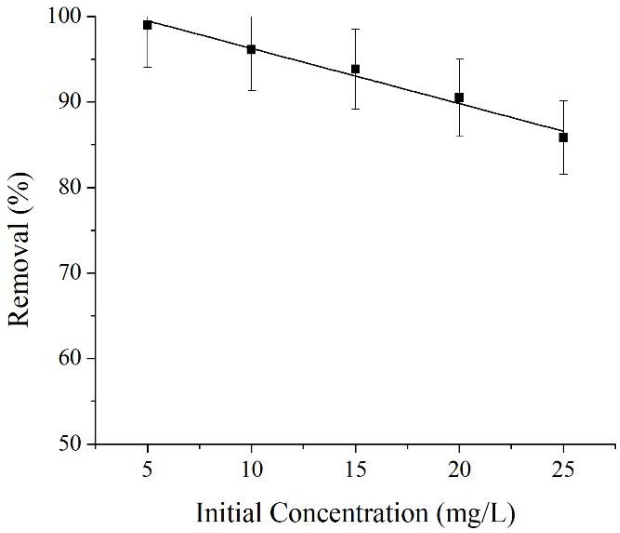

Fig. 4. Effect of DCS concentration on removal efficiency of DCS by GNP. Shaker speed: 150 rpm, contact time = 40 min, initial pH = 5 ± 0.1, temperature = 25°C, and GNP dosage = 3.5 g/L.

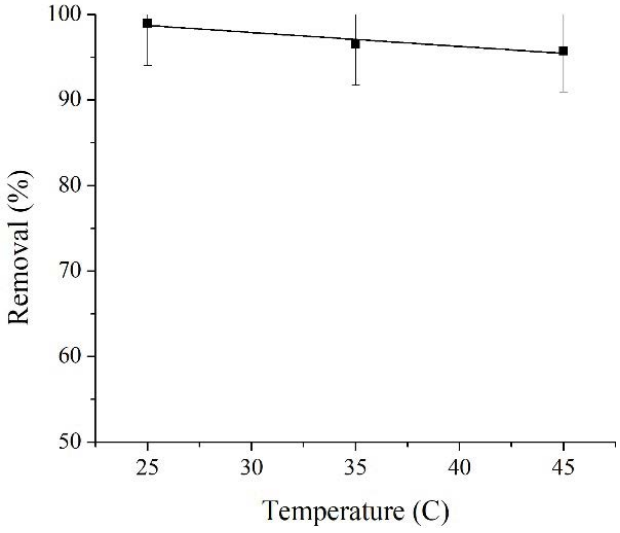

Fig. 5. Effect of temperature on removal efficiency of DCS by GNP. Shaker speed: 150 rpm, contact time = 40 min, initial pH = 5 ± 0.1, GNP dosage = 3.5 g/L, and initial concentration of DCS = 5 mg/L.

where Q_e (mg/g) is the amount of DCS adsorbed per gram of GNP, C_0 and C_e are the concentrations (mg/L) of DCS before and after the adsorption study, respectively, vis the volume of the solution in liters, and m is the mass of GNP in grams.

Three isotherm models were used to fit the experimental data; Langmuir, Freundlich, and Temkin. The Langmuir isotherm model assumes monolayer adsorption without any lateral interactions between molecules of adsorbate on the surface. On the other hand, Freundlich isotherm model remove the assumption of the none existence of adsorbate–adsorbate interaction on the surface. Whereas

in Temkin model, the linear decrease in heat of sorption is the main assumption that opposes the logarithmic decrease implied in the model given by Freundlich [24,25]. The linearized equations for Langmuir, Freundlich, and Temkin are given in Eqs. (3)–(5), respectively:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m K_L} \tag{3}$$

$$\log Q_e = \log K_F + \frac{1}{n}\log C_e \tag{4}$$

$$Q_e = B \ln K_T + B \ln C_e \tag{5}$$

where Q_m (mg/g) is the maximum adsorption capacity, K_L (L/mg) is the Langmuir isotherm parameter, K_F (mg$^{(1-1/n)}$ L$^{1/n}$g^{-1}), and n are the Freundlich isotherm parameters and B (J/mol) and K_T (L/mg) are Temkin isotherm parameters. Figs. 6a–c show the graphical depiction of Langmuir, Freundlich, and Temkin isotherm models, respectively. The results obtained show regression coefficients (R^2) of 0.9967, 0.9763, and 0.9777, respectively. Hence, the Langmuir model was found to best fit the experimental data in this work. The parameters of all three models are summarized in Table 1, with a Langmuir maximum adsorption capacity of 8.34 mg/g.

When comparing the results of this study to a literature overview of different carbon-based adsorbents used for the removal of DCS (Table 2), it can be observed that generally the adsorption capacity for DCS is low. Although, high adsorption capacities were observed through the modification of graphene surfaces in several studies, generally the adsorption capacity is low and comparable to the values found in this study. Thus, the surface modified derivatives of graphene could possibly be more efficient in the removal of DCS from water. However, the use of graphene is more

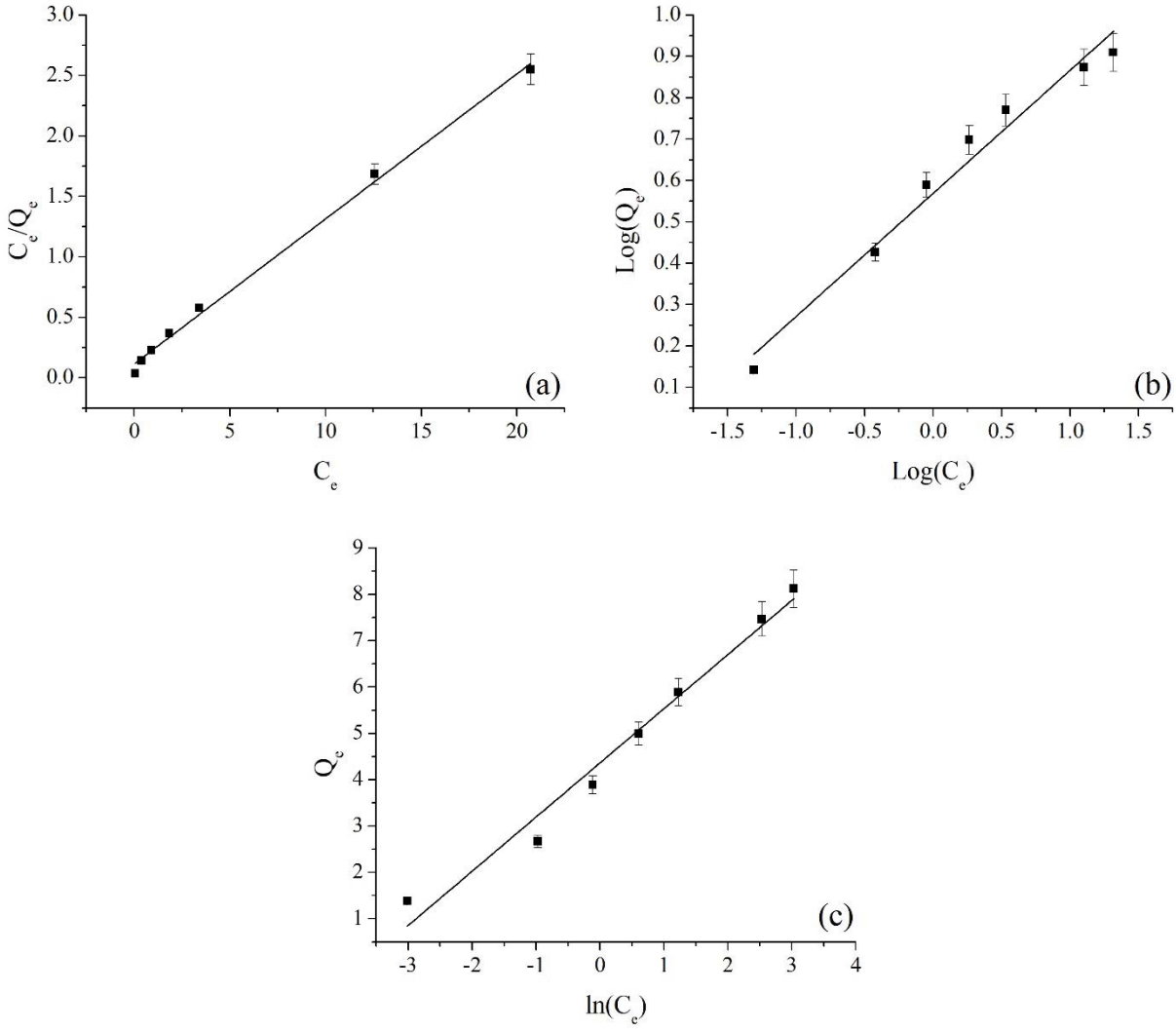

Fig. 6. Adsorption isotherm models for DCS removal (a) Langmuir isotherm model, (b) Freundlich isotherm model, and (c) Temkin isotherm model. Experimental conditions: shaker speed: 150 rpm, contact time = 40 min, initial pH = 5 ± 0.1, GNP dosage = 3.5 g/L, temperature = 25°C.

Table 1
Adsorption parameters for DCS removal

Model	Adsorption Parameters	
Langmuir	K_L	1.0363
	Q_m	8.3402
	R^2	0.9967
Freundlich	K_F	3.7068
	n	3.3624
	R^2	0.9763
Temkin	B	1.1696
	K_T	41.768
	R^2	0.9777

effective in terms of cost and commercialized usability due to its wide availability.

3.3. Adsorption kinetics

Pseudo-first-order and pseudo-second-order models are the most commonly used kinetic models applied to adsorption processes [34]. Both models were applied to understand the kinetics of DCS adsorption on GNP. The linearized mathematical expressions for pseudo-first and pseudo-second-order models are given in Eqs. (6) and (7), respectively.

$$\ln\left(Q_e - Q_t\right) = -K_1 t + \ln Q_e \tag{6}$$

$$\frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{K_2 Q_e^2} \tag{7}$$

where Q_t (mg/g) is the amount of DCS adsorbed on GNP at any time t, while K_1 (1/min) and K_2 (g/mg min) are the pseudo-first and pseudo-second-order rate constants, respectively. The kinetic rate constants were obtained, after plotting the data according to the model as mentioned earlier (Fig. 7). The observed regression coefficient (R^2) for the pseudo-second-order was far better than the one obtained from pseudo-first-order plot (Table 3). Hence, it can be concluded that the adsorption process of DSC by GNP is governed by pseudo-second-order reaction kinetics. The rate constants and R^2 values for both models are summarized in Table 3.

Table 3
Kinetic model parameters for DCS removal

Model	Adsorption parameters	
Pseudo-first-order	K_1	0.065
	Q_e	24.38
	R^2	0.630
Pseudo-second-order	K_2	1.822
	Q_e	1.340
	R^2	0.999

3.4. Adsorption thermodynamics

Calculation of different thermodynamic properties such as the Gibbs free energy change ($\Delta G°$), change in enthalpy ($\Delta H°$), and change in entropy ($\Delta S°$) are vital to study the feasibility, spontaneity, and thermal nature of the adsorption process [18]. To calculate the thermodynamic properties, Sip's equation [35] was used. The mathematical expression is given in Eq. (8).

$$Q_e = Q_e^{\text{th}} \frac{K_{\text{eq}} C_e^{n_s}}{1 + K_{\text{eq}} C_e^{n_s}} \tag{8}$$

where Q_e^{th} (mg/g) is the maximum theoretical capacity and n_s is the Sips constant. Eq. (8) was used to estimate the equilibrium constant, K_{eq} at different temperatures. Once the value of Q_e^{th}, n_s, and K_{eq} was determined after regression analysis, the Van't Hoff plot was obtained, and it is shown in Fig. 8. The values of the parameters calculated are shown in Table 4. The change in Gibbs free energy was calculated using Eq. (9) [36].

$$\Delta G° = -RT \ln K_{\text{eq}} \tag{9}$$

Table 2
Comparison of different adsorbents used for the removal of DCS

S. No.	Adsorbent	Maximum adsorption capacity (mg/g)	Reference
1	Carbon nanotubes (CNT)	27	[26]
2	Commercial activated carbon	76	[17]
3	Activated carbon (AC) derived from cocoa shell	63	[27]
4	Single layered graphene oxide (GO)	750.0	[28]
5	Reduced graphene oxide (rGO)	59.67	[29]
6	3D graphene aerogel	596.71	[30]
7	CTAB-ZIF-67	54.31	[31]
8	CNT/HNO_3	24	[32]
9	AC derived from olive stones	11	[33]
10	Graphene nanoplatelets	8.34	This study

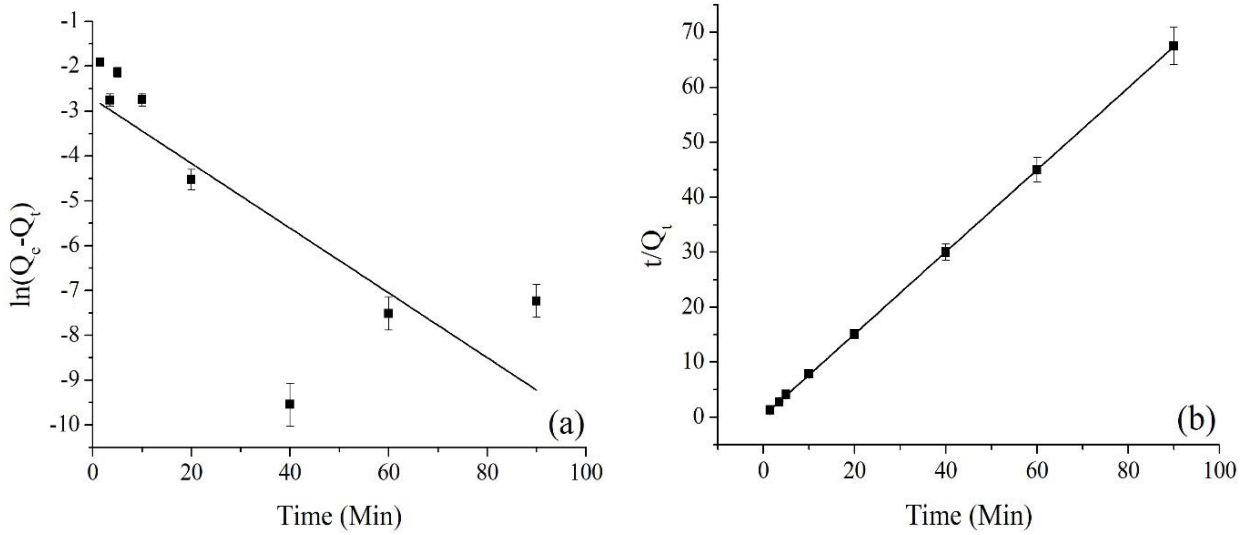

Fig. 7. Kinetic models for DCS removal (a) pseudo-first-order kinetic model and (b) pseudo-second-order kinetic model. Experimental conditions: shaker speed: 150 rpm, initial pH = 5 ± 0.1, GNP dosage = 3.5 g/L, initial concentration 5 mg/L, temperature = 25°C.

Table 4
Calculated Sips parameter at different temperature

Temperature (K)	K_{eq}	n_s	Q_e^{th} (mg/g)
298.1	20.260 (±1.013)	0.295 (±0.014)	7.918 (±0.396)
308.1	18.962 (±0.950)	0.360 (±0.018)	14.78 (±0.739)
318.1	18.352 (±0.918)	0.371 (±0.019)	15.07 (±0.753)

where R (J/mol K) is the general gas constant, and T (K) is the temperature. The values of other thermodynamic parameters were calculated using the Van't Hoff equation as given by Eq. (10).

$$\ln K_{eq} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{10}$$

The values of thermodynamic properties obtained are given in Table 5. The value of Gibbs free energy shows that the process of adsorption is physical in nature (between –20 and 0 KJ/mol) [34] while the negative sign is an indication of spontaneous nature of the process. Moreover, the negative value of enthalpy (ΔH°) implies that the adsorption is exothermic in nature as predicted in section 3.1.5 (Effect of temperature).

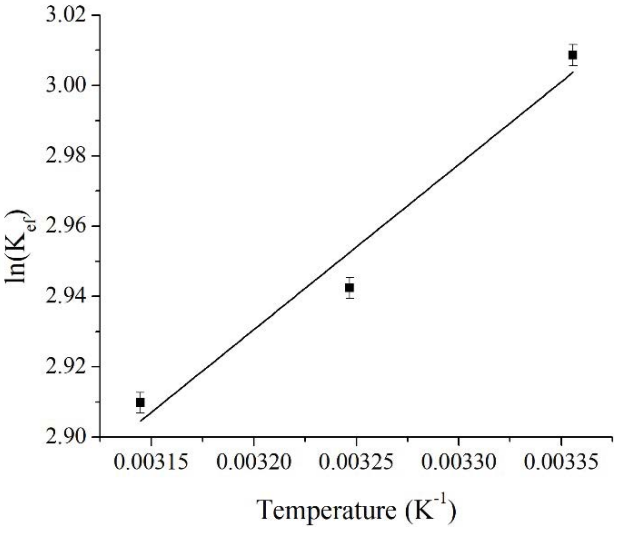

Fig. 8. Van't Hoff plot for DCS removal.

4. Conclusions

GNP showed good efficiency in the removal of DCS. The equilibrium time and dosage were found to be 40 min and 3.5 g/L, respectively. It was observed that the best removal occurs in acidic media (pH < 5) and smaller drug concentration. In addition, the removal is slightly decreased with increasing temperature. Langmuir isotherm was the best-fit model for the adsorption of DCS with maximum adsorption capacity of 8.34 mg/g. The process was found to follow pseudo-second-order kinetics. The values of Gibbs free energy (ΔG°) and enthalpy change (ΔH°) were negative confirming the spontaneity and the exothermic nature of the adsorption process. The results of this study show that due to its high surface area and excellent adsorptive properties, GNP show a promising tool as an adsorbent for the removal of DCS in water.

Table 5
Thermodynamic properties

	$\Delta G°$		$\Delta H°$	$\Delta S°$
	kJ/mol		kJ/mol	J/mol K
298.1 K	308.1 K	318.1 K		
–7.458 (±0.373)	–7.294 (±0.365)	–7.213(±0.360)	–3.910 (±0.195)	11.856 (±0.593)

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