Adsorption of 4th Generation Antibiotics using Graphene

A Combined Experimental and Theoretical Study

Thaiyal Nayahi.V. A. N
Department of Environmental Engineering,
University College of Engineering (BIT Campus),
Campus), Tiruchirapalli, India

Lavanya. M
Department of Environmental Engineering,
University College of Engineering (BIT
Tiruchirapalli, India

***Abstract*—This study explores the removal of 4th generation antibiotics like Cefclidine, Cefepime, Cefoselis, Cefluprenam, Cefozopran, Cefpirome and Cefquinome which are considered as harmful pharmaceutical pollutants. Graphene is used as an adsorbent to remove these pharmaceutical compounds. In this, graphene was produced by electrochemical exfoliation method. This synthesised graphene was used as an adsorbent material for the removal of 4th generation antibiotics from the prepared synthetic pharmaceutical sample. The effects of contact time, concentration, pH and temperature were studied. The adsorption kinetics was modelled by pseudo first and second order kinetics, Elovich and Weber and Morris intraparticle diffusion models. The rate constants for all these kinetic models were calculated and the results show that the second order kinetic models were best fitted to model the kinetic adsorption of 4th generation antibiotics. The Langmuir, Freundlich, D–R isotherm and Temkin models were applied to describe the equilibrium isotherms and the isotherm constants were determined. The adsorption was studied thermodynamically, and the Gibbs free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) were calculated. Thus the study indicates graphene could be a very efficient adsorbent for the removal of 4th generation antibiotics.**

***Keywords*—Removal; antibiotics; graphene; kinetics; isotherms; thermodynamics.**

I.INTRODUCTION

Pharmaceutical pollutants are considered as a major impending deleterious pollution that contains different groups of human and veterinary medicinal compounds that are used extensively all over the world. Due to their very low concentrations they are impalpable, cause chronic effects on ecosystems and the totality of their impacts on the aquatic environment over the long term is difficult to predict. Pharmaceutical compounds are resistant to biological degradation and retain their chemical structure long enough to do their adverse effect [1]. The most frequently found pharmaceutical pollutants in the water are antibiotics, antacids, steroids, antidepressants, analgesics, and stimulants. Cephalosporins are considered as the most commonly used antibiotics. They are grouped into "generations" by their antimicrobial properties. In that, 4th generation antibiotics are considered as the upcoming pollutant. Many fourth generation cephalosporins can cross blood brain barrier and are effective in meningitis [2]. The fourth generation includes: Cefclidine, Cefepime, Cefluprenam, Cefoselis**,** Cefozopran**,** Cefpirome and Cefquinome. Pharmaceutical pollution doesn't seem to be harming humans yet [3], but disturbing clues from aquatic life suggests, now is the time for preventive action. Some of the methods that are used to remove pharmaceutical compounds from water stream are constructed wetland, activated sludge treatment, photocatalytic oxidation or adsorption [4-7]. Of the above mentioned methods, adsorption is the most promising method for the removal of pollutants because both water and the adsorbent could be recycled, and no by-products would be produced [8]. Hence, scientists continuously search for new types of adsorbents which can remove the pollutants efficiently.

Graphene is a new fascinating carbon material that has engrossed the attention of scientist in recent years. It is a one atom-thick, two-dimensional (2D) layer of sp^2-bonded carbon. Graphene also exhibits extraordinary properties, such as excellent mechanical, electrical, thermal, optical properties and very high specific surface area. Additionally, graphene has also been used as an excellent adsorbent for different pollutants due to its large surface areas, which can form strong interactions with other pollutants [9-13]. In this study, synthesised graphene was used to adsorb a group of 4th generation antibiotics.

The effects of different adsorption conditions were studied: contact time, solution concentration, pH and temperature. Additionally, the adsorption process was studied kinetically to predict the adsorption rate in order to understand the adsorption behaviour. Then the adsorption was studied thermodynamically to understand the mechanism of adsorption and its spontaneity by calculating different thermodynamic parameters.

II. MATERIALS AND METHOD

A. Synthesis of graphene

The electrochemical synthesis of graphene from graphite was done by electrochemical exfoliation method. During the exfoliation process the highly oriented pyrolytic graphite (HOPG; 3 cm x 3 cm x 0.5 mm) was employed as an electrode and source of graphene for electrochemical exfoliation. Two graphite electrodes were immersed into the 0.5 M sulphuric acid (sigma Aldrich 98%) solution. Both anode and cathodes was graphite electrode. The

electrochemical exfoliation process was carried out by applying DC bias on graphite electrode (from +10 V). Due to anodic dissolution, a few layers of graphene were exfoliated from the graphite anode. By this way the exfoliated graphene sheets were collected with a 100 nm porous filter and washed with DI water by vacuum filtration. After drying, it was dispersed in DMF solution by gentle water-bath sonication for 10 min to remove the unwanted large graphite particles produced in the exfoliation. The suspension was subjected to centrifugation at 2500 rpm. The centrifuged suspension can be used for further adsorption experiments.

B. *Preparation of synthetic pharmaceutical sample*

Cefclidine, Cefepime, Cefoselis, Cefluprenam, Cefozopran, Cefpirome and Cefquinome were dissolved in distilled water for the required concentration (0.5-2.5 mg L^{-1}) to obtain synthetic pharmaceutical sample for further experiments. The pH of the solution was adjusted to 7 using NaOH and HCl.

C. *Batch adsorption studies*

Batch adsorption experiments were conducted using 200 ml glass beaker with addition of 0.1 g of graphene and 100 ml of prepared synthetic pharmaceutical solutions for 7 compounds of concentration from 0.5 – 2.5 mg L^{-1}. The glass beakers are then placed on a stirrer under a suspension of 200 rpm, 30°C for 90 minutes. Similarly, experiments were carried for different pH (1-13) and antibiotics concentration at 2.5 mg L^{-1}. The concentration of antibiotic compounds in synthetic pharmaceutical solution was determined by measuring the solution at λ=230 nm using indirect UV method. To study the effect of temperature on adsorption, adsorption measurement was carried at different temperatures (303, 313, 323, 333, 343 and 353 K). Antibiotics uptake was calculated according to the following equation:

$$q_t = \frac{(C_0 - C_t).V}{W} \qquad (1)$$

Adsorption efficiency was calculated according to the following equation:

$$\text{Adsorption efficiency} = \frac{C_o - C_e}{C_o} \times 100 \qquad (2)$$

where q_t is the amount (mg g^{-1}) of antibiotics adsorbed at time t, C_0 is initial concentration (mg L^{-1}) of antibiotic compounds in aqueous solution, C_t is the concentration of antibiotic compounds at time t (mg L^{-1}), V is the volume (L) of the adsorbate solution, and W is the weight (g) of dried graphene.

After reaching the equilibrium time, the concentration of antibiotics in solution at equilibrium, C_e, was determined and the concentration in the solid phase, q_e, was calculated using Equation (1). Kinetic experiment were modelled through pseudo first order equation [16] and pseudo second order [17] equation, Elovich [18] and Weber and Morris [19] equation. Experimental data were modelled through Langmuir [20], Freundlich [21], D-R [22] and Temkin [23] models.

III. RESULTS AND DISCUSSION

A. *Effect of pH*

The pH is one of the most important parameter that controls the adsorption efficiency and capacity. To examine this effect, a series of experiments were carried out using 2.5mg L^{-1} of 4th generation antibiotics containing synthetic pharmaceutical solutions. The relation between the initial pH of the solution and adsorption efficiency of pharmaceutical compounds is depicted in Fig. 1. The effect of pH on the removal of 4th generation antibiotics using 0graphene as an adsorbent was studied with initial pH range from 1-13. The optimum 4th generation antibiotics adsorption was observed at pH range 6.0–8.0. We have observed that the percentage adsorption of 4th generation antibiotics increased appreciably with increase of pH from 1 to 8 and then the adsorption efficiency starts to decrease with increase in pH after 8 [14]. The lower adsorption of 4th generation antibiotics at alkaline pH might be due to the electrostatic repulsion of 4th generation antibiotics by the negatively charged graphene surface at high pH. The adsorption capacity increases with pH in the acidic range and reaches the maximum removal efficiency. This is found to be appropriate in all the 7 4th generation antibiotic compounds.

B. *Effect of contact time and concentration*

In order to establish time dependence of 4th generation antibiotics adsorption under various concentrations, it is required to study the influence of contact time. From Fig. 2, it is clear that the adsorption of 4th generation antibiotics is increased with an increase in time and remains stable after the equilibrium time. The equilibrium time was 60 min for all the concentrations (0.5-2.5 mg L^{-1}) and for all the 7 compounds.

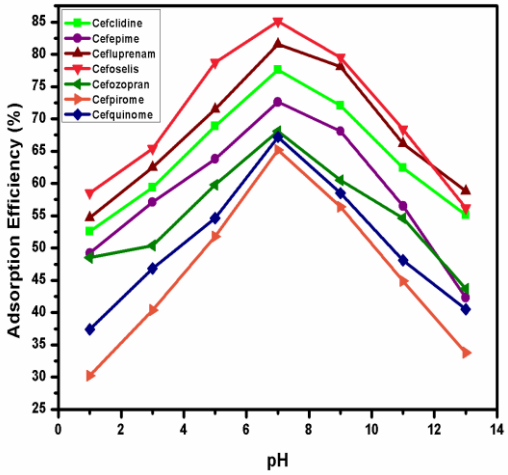


Fig. 1 The effect of initial pH on 4th generation antibiotics adsorption by graphene. Conditions: concentration= 2.5 mg L^{-1}

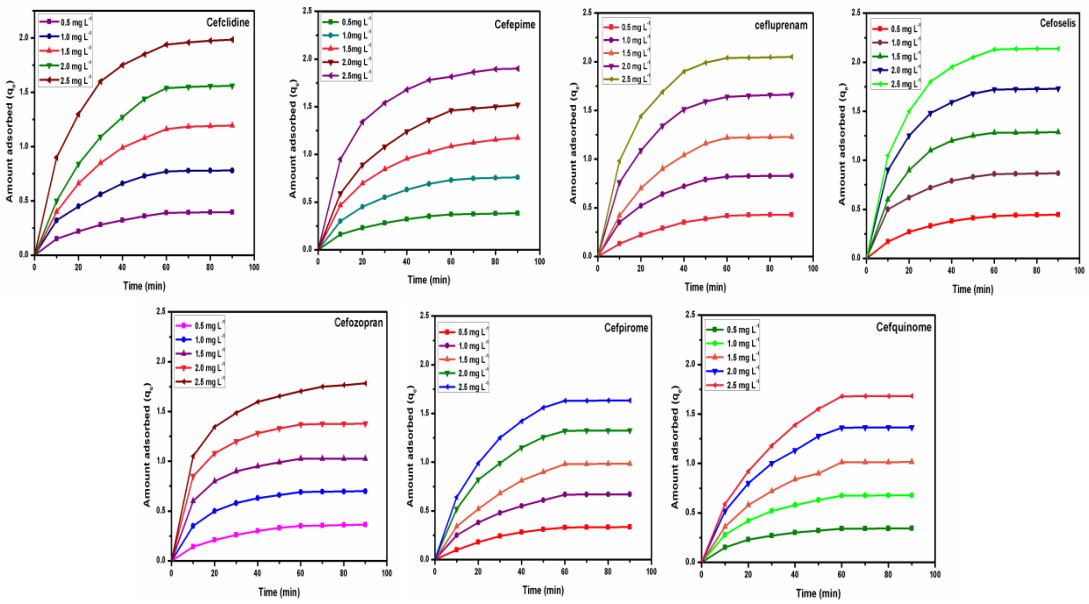


Fig. 2 The effect of agitation time and concentration of 4th generation antibiotics adsorbed on graphene.
Conditions: concentration = 0.5-2.5 mg L ^{1}; pH=7.0; temperature= 303 K

The rapid adsorption is observed during the first 60 min. After 60 min, adsorption is almost found to be stagnant. This rapid initial adsorption was due to the availability of large graphene surface for antibiotic molecules at initial stages. This rapid adsorption decreases gradually until all graphene surfaces are occupied and a constant rate of adsorption is observed. The plots are single, smooth and continuous curves leading to saturation for all the 7 compounds.

C. Effect of temperature

Temperature has an important effect on the adsorption process. As the temperature increases, rate of diffusion of adsorbate molecules across the external boundary layer and interval pores of the adsorbent particle increases [15]. Enhancement of the adsorption capacity of adsorbent (graphene) at higher temperatures may be attributed to the enlargement of pore size and/or activation of the adsorbent surface. The effect of temperature for adsorption of 4th generation antibiotics on graphene was premeditated at various temperatures (303, 313, 323, 333, 343 and 353 K). Fig. 3 illustrates that the adsorption capacity increases with increases in temperature and thus confirms the endothermic nature of adsorption process. The enhancement in uptake is attributed to better interaction between ions and adsorbent, creation of new adsorption sites and increased intraparticle diffusion at higher temperatures [15]. Therefore, the adsorption becomes more favourable in all the 7 compounds.

D. Adsorption kinetics model

The studies of adsorption equilibrium are important in determining the effectiveness of adsorption; however, it is also necessary to identify the types of adsorption mechanism in a given system. In this study we used four different models to predict the adsorption kinetics of 4th generation antibiotics on graphene. In the present study, four kinetic models, namely, pseudo first order, pseudo second order, Elovich and Weber and Morris intraparticle diffusion models were examined to obtain the rate constants, equilibrium adsorption capacity and adsorption mechanism at different concentrations of all the 7 compounds of 4th generation antibiotics.

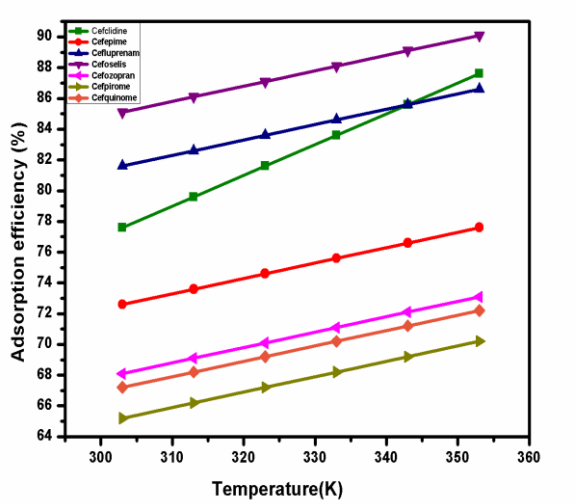


Fig. 3 The effect of adsorption efficiency of 4th generation antibiotics on graphene at various temperatures (303, 313, 323, 333, 343 and 353 K).
Conditions: concentration=2.5 mg L $^{-1}$; pH=7.0.

		q_e (exp) (mg g^{-1})	FIRST ORDER KINETICS			SECOND ORDER KINETICS		
			q_e (Cal) (mg g^{-1})	K_1 (min^{-1})	R^2	q_e (Cal) (mg g^{-1})	K_2 (min.g mg^{-1})	R^2
Cefclidine	0.5	0.39	5.88	0.1124	0.5749	0.37	0.07733	0.9898
	1.0	0.77	3.31	0.0713	0.4930	0.74	0.04678	0.9911
	1.5	1.16	3.93	0.0612	0.4362	1.11	0.02257	0.9913
	2.0	1.54	3.47	0.0401	0.3157	1.45	0.01138	0.9818
	2.5	1.94	4.78	0.0559	0.3738	1.9	0.01584	0.9979
Cefepime	0.5	0.37	2.87	0.09476	0.5036	0.36	0.1071	0.9959
	1.0	0.73	3.41	0.07719	0.5045	0.71	0.04806	0.9959
	1.5	1.085	3.31	0.06153	0.4352	1.125	0.03171	0.9997
	2.0	1.46	4.37	0.05739	0.4182	1.41	0.02280	0.9963
	2.5	1.815	3.58	0.05158	0.3232	1.81	0.03703	0.9941
Cefluprenam	0.5	0.415	3.69	0.09446	0.5565	0.4	0.04848	0.9801
	1.0	0.82	5.87	0.09661	0.5131	0.79	0.06826	0.9929
	1.5	1.22	10.1	0.09617	0.4693	1.16	0.02465	0.9922
	2.0	1.64	5.51	0.07279	0.4187	1.6	0.03540	0.9946
	2.5	2.04	6.68	0.07176	0.3031	2.01	0.03465	0.9949
Cefoselis	0.5	0.43	3.36	0.09666	0.5362	0.42	0.08485	0.9945
	1.0	0.86	6.57	0.10635	0.5262	0.83	0.1033	0.9998
	1.5	1.28	7.52	0.09875	0.4647	1.25	0.0559	0.9938
	2.0	1.72	7.44	0.08667	0.4597	1.69	0.04925	0.9969
	2.5	2.13	8.62	0.08302	0.4703	2.07	0.03415	0.9963
Cefozopran	0.5	0.35	3.93	0.1052	0.5515	0.34	0.09589	0.9947
	1.0	0.69	5.09	0.1029	0.5424	0.7	0.1069	0.9980
	1.5	1.026	21.9	0.4118	0.5554	1.001	0.1107	0.9986
	2.0	1.37	6.75	0.09742	0.5187	1.34	0.08652	0.9991
	2.5	1.703	3.51	0.05769	0.4122	1.705	0.05517	0.9998
Cefpirome	0.5	0.33	6.979	0.1232	0.55174	0.31	0.07	0.9716
	1.0	0.667	9.82	0.1122	0.55249	0.63	0.04652	0.9892
	1.5	0.981	11.47	0.107	0.54424	1.2	0.03947	0.9931
	2.0	1.322	12.07	0.1025	0.49591	1.3	0.0303	0.9899
	2.5	1.63	13.04	0.0991	0.47589	1.6	0.02467	0.9888
Cefquinome	0.5	0.34	6.55	0.1273	0.57609	0.33	0.1553	0.9958
	1.0	0.675	9.21	0.1141	0.54812	0.64	0.0635	0.9934
	1.5	1.011	12.07	0.1051	0.5404	0.95	0.02896	0.9885
	2.0	1.362	11.12	0.1008	0.5035	1.3	0.02521	0.9890
	2.5	1.68	14.75	0.0961	0.49159	1.67	0.01626	0.9839

Table 1 A comparison between the experimental and calculated q_e values for different concentrations in first and second order adsorption kinetics of 4th generation antibiotics on graphene, temperature of 303 K and pH 7

a. First order lagergren model.

The first order Lagergren model is generally expressed as follows [16]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (3)$$

where q_e and q_t are the adsorption capacities at equilibrium at time t (mg g^{-1}) and the adsorption capacities at time t (min) respectively, and k_1 (min) is a rate constant of first order adsorption. The integrated form of the above equation with the boundary conditions (t = 0 to t and q_t = 0 to q_t) is rearranged to obtain the following time dependence function:

$$\log (q_e - q_t) = \log q_t - \frac{k_1}{2.303} t \qquad (4)$$

The experimental data were analyzed initially with the first order Lagergren model. The plot between log (q_e - q_t) vs. t should give the linear relationship from which k_1 and q_e can be determined by the slope and intercept, respectively (eqn (4)). The computed results are presented in Table 1. The results show that the theoretical q_e (cal) value doesn't agree with the experimental q_e (exp) values for all

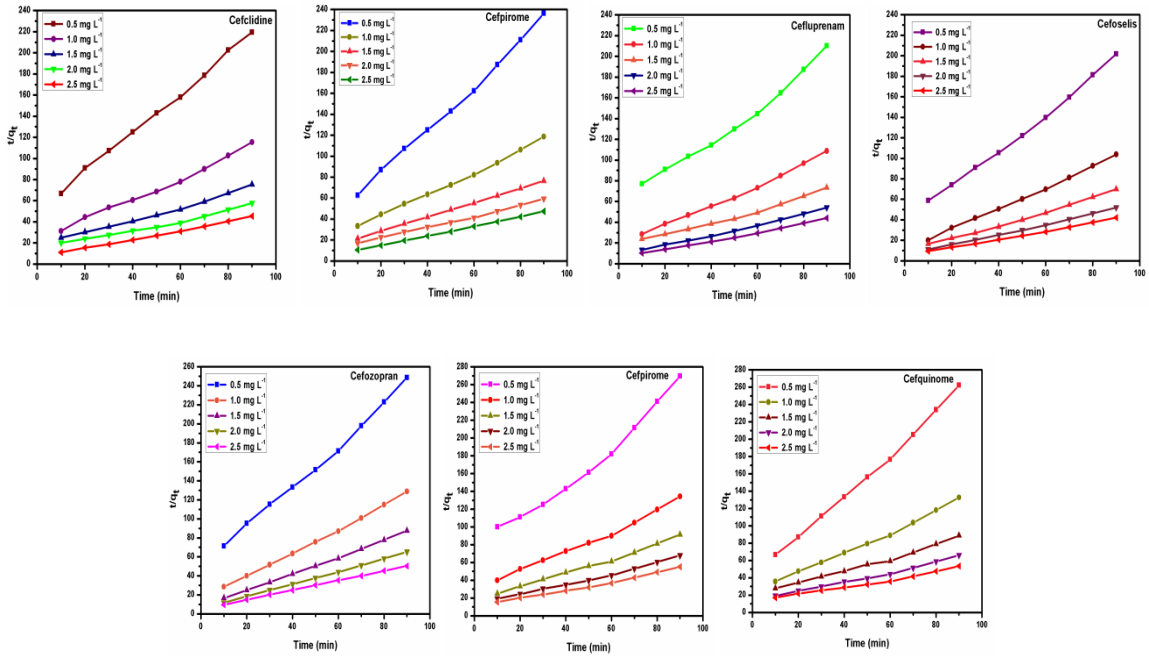


Fig. 4 Adsorption kinetics of 4th generation antibiotics adsorption by graphene for the pseudo-second order model. Conditions: concentrations = 0.5-2.5 mg L^{-1}; pH = 7.0; temperature= 303 K

concentrations and compounds studied and with a poor correlation co-efficient.

b. Second order lagergren model

The Lagergren second order kinetic model is generally expressed as follows [17]:

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \qquad (5)$$

where k_2 is rate constant of second order adsorption. The integrated form of eqn (5) with the boundary condition (t = 0 to t) and (q = 0 to q_t) is

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \qquad (6)$$

Eqn (6) can be rearranged and linearized as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (7)$$

where qe and qt are the amount of 4th generation antibiotics adsorbed on graphene at equilibrium time t and at time t (min) respectively, and k_2 is the rate constant for the second order kinetic model. The kinetic data were fitted to the second order Lagergren model (eqn (7)). The equilibrium adsorption capacity, q_e (cal) and k_2 were determined from the slope and intercept of plot of t/q_t vs. t (Fig. 4) and are tabulated in Table 1. The plots were found to be linear with good correlation coefficients. The theoretical q_e (cal) values agree well with the experimental q_e (exp) values. This implies that in all the 7 compounds and in all the concentrations, the second order models are well-suited with the experimental data's and can be used to favourably explain the 4th generation antibiotics adsorption on graphene.

c. Elovich model

The Elovich model equation is generally expressed as follows [18]:

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \qquad (8)$$

The simplified form of Elovich (eqn (6)) is

$$q_t = \frac{1}{b} \ln (ab) + \frac{1}{b} \ln (t) \qquad (9)$$

where a is the initial adsorption rate (mg g^{-1} min^{-1}) and b is the desorption constant (g mg^{-1}). The Elovich model was tested for the 4th generation antibiotics adsorbed kinetic values. A plot between q_t vs. ln (t) should yield a linear relationship with the slope of (1/b) and an intercept of 1/b ln (ab) and values of a and b are calculated using (eqn (9)). Table 2 depicts the results obtained from the Elovich equation. The lower regression value shows the inapplicability of this model.

d. Weber and Morris intraparticle diffusion model

With the aim of nearing into the mechanisms and rate controlling steps affecting the kinetics of adsorption, the kinetic results were analysed by the intraparticle diffusion model to elucidate the diffusion mechanism, whose model is expressed as follows [19]:

POLLUTANT	ELOVICH MODEL			INTRAPARTICLE DIFFUSION MODEL	
	a (mg g $^{-1}$ min $^{-1}$)	b (mg g^{-1})	R^2	k_p (mg g $^{-1}$ min$^{-1/2}$)	R^2
Cefclidine	0.3350	1.9395	0.9680	0.1686	0.8866
Cefepime	0.4508	2.2905	0.9680	0.1426	0.8866
Cefluprenam	0.4406	2.0029	0.9301	0.1609	0.8235
Cefoselis	0.4896	1.9630	0.9391	0.1645	0.8364
Cefozopran	0.8931	2.9985	0.9817	0.1095	0.9096
Cefpirome	0.2024	2.0651	0.9541	0.1575	0.8711
Cefquinome	0.1630	1.8337	0.9665	0.1803	0.9081

Table 2 Elovich and Intraparticle diffusion model for 4th generation antibiotics at temperature 303 K, temperature 2.5 mg L $^{-1}$ and pH 7.

$$q_t = k_p t^{1/2} + C \qquad (10)$$

where C is the intercept and k_p is the intra-particle diffusion rate constant (mg g $^{-1}$ min$^{-1/2}$), which can be evaluated from the slope of the linear plot between q_t vs. $t^{1/2}$. The intercept of the plot reflects the boundary layer effect. The larger the intercept, the greater contribution of the surface adsorption in the rate controlling step. If the regression of q_t vs. $t^{1/2}$ is linear and passes through the origin, then intraparticle diffusion is the sole rate-limiting step. Lower and higher values of k_{id} illustrate an enhancement in the rate of adsorption and better adsorption with improved bonding between the pollutant and the adsorbent particles, respectively. However, the linear plots at each concentration did not pass through the origin. This indicates that the intra-particle diffusion was not only rate controlling step. The results are presented in Table 2.

The tables 1 and 2 depict the computed results obtained from first order, second order, Elovich and Weber and Morris intraparticle diffusion. From the tables, it is found that the adsorption follows the second order model rather than the other models. Furthermore, the calculated q_e values agree well with the experimental q_e values for the second order kinetics model, concluding that the second order kinetics equation is the best fitting kinetic model for all the 7 compounds.

E. Adsorption isotherm

The quantity of adsorbate that can be taken up by an adsorbent is a function of both the characteristics concentration of adsorbate and temperature. The characteristics of the adsorbate that are of importance include: solubility, molecular structure, molecular weight, polarity and hydrocarbon. Generally, the amount of material adsorbed is determined as a function of the concentration at a constant temperature, and the resulting function is called adsorption isotherm [20].

In this, the widely used Freundlich, Langmuir, D–R isotherm and Temkin models are applied to simulate and understand the adsorption mechanism of 4th generation antibiotics at various concentrations.

a. Langmuir isotherm

The Langmuir model assumes monolayer coverage on the adsorbent. The linearized form of the Langmuir adsorption isotherm model is as follows [21]:

$$\frac{1}{q_e} = \frac{1}{K_a q_m}\left(\frac{1}{C_e}\right) + \frac{1}{q_m} \qquad (11)$$

where q_e is amount adsorbed (mg g $^{-1}$) at equilibrium concentration C_e (mg L^{-1}), q_m is the Langmuir constant representing maximum monolayer adsorption capacity (mg g $^{-1}$) and K_a is the Langmuir constant related to energy of adsorption.

The Langmuir isotherm constants K_a and q_m were calculated from the slope and intercept of the plot between $1/q_e$ vs. $1/C_e$ (Fig. 5). The Langmuir model parameters and the statistical fits of the adsorption data to this equation are given in Table 3. As from Table 3, the higher regression coefficient confirmed that the Langmuir isotherm best represented the equilibrium adsorption of 4th generation antibiotics to grapheme at various concentrations. The excellent fit of the Langmuir isotherm to the experimental data at all temperatures were studied, confirmed that the adsorption is monolayer; adsorption of each molecule had equal activation energy and that adsorbent–adsorbate interaction was negligible.

POLLUTANT	Langmuir adsorption Isotherm				Freundlich adsorption isotherm		
	q_m (mg g^{-1})	K_a (L mg^{-1})	R^2	R_L	K_f (L mg^{-1})	N	R^2
Cefclidine	23.040	0.1556	0.9987	0.9763	3.344	1.019	0.9985
Cefepime	14.720	0.1974	0.9990	0.6696	2.510	1.092	0.9965
Cefluprenam	12.485	0.4020	0.9981	0.4987	4.208	1.058	0.9981
Cefoselis	35.65	0.1746	0.9993	0.6961	5.688	1.032	0.9978
Cefozopran	12.899	0.1853	0.9995	0.6834	2.106	1.054	0.9998
Cefpirome	89.92	0.0217	0.9982	0.9484	1.898	1.021	0.9982
Cefquinome	45.43	0.1853	0.9996	0.8948	2.069	1.012	0.9992

Table 3 Langmuir and Freundlich adsorption isotherm for 4th generation antibiotics at temperature 303K and pH 7.

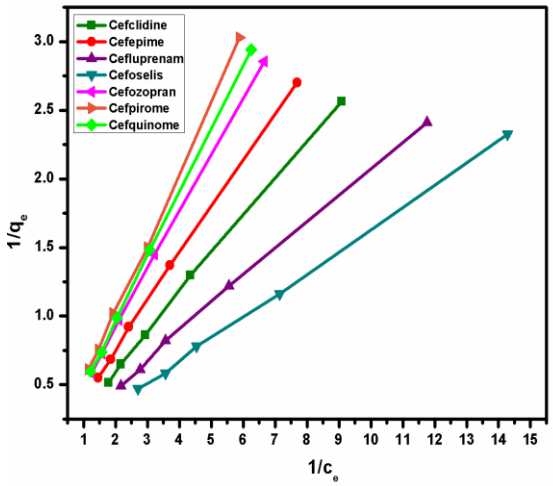


Fig. 5 A Langmuir plot ($1/q_e$ vs. $1/C_e$) for 4th generation antibiotics adsorption by graphene. Conditions: pH = 7.0; temperature = 303 K and concentration = 0.5-2.5 mg L^{-1}

The essential characteristics of the Langmuir isotherm can be expressed as the dimensionless constant R_L [21]:

$$R_L = \frac{1}{1+K_a C_o} \qquad (12)$$

where R_L is the equilibrium constant and it indicates the type of adsorption, K_a is the Langmuir constant and C_o is the various concentrations of 4th generation antibiotics. R_L gives a qualitative measure of the favourability of the adsorption process; if R_L greater than 1, it indicates unfavourable adsorption and if R_L is between 0 to 1, it indicates the favourable adsorption. From the study R_L ranges from 0 to 0.97. This suggests that the adsorption is favourable.

b. Freundlich isotherm

Freundlich model is an empirical model allowing for multilayer adsorption on adsorbent. The linearized logarithmic form and the Freundlich constants can be expressed as follows [22]:

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \qquad (13)$$

where k_f is the Freundlich constant related to adsorption capacity (L mg $^{-1}$), n is the energy or intensity of adsorption, C_e is the equilibrium concentration of nitrate (mg L^{-1}). The values of k_f and 1/n obtained from the intercept and slope from a plot between log q_e vs. log C_e, are shown in Fig. 6. The values are specified in Table 3. The values of 1/n was less than unity, suggesting that 4th generation antibiotics was adsorbed favourably by graphene at all concentrations studied.

Table 3 shows that the adsorption of 4th generation antibiotics onto graphene had a higher regression coefficient for determination of Langmuir isotherm and Freundlich isotherm. The dimensionless constant R_L was calculated from Eqn. (12). The R_L values were found to lies between 0 and 1 for all the concentrations. The n values lies between 1 and 10 for all the concentrations. From the table 3, this study obeys both Langmuir and Freundlich isotherm.

c. Dubinin–Radushkevich isotherm

Dubinin–Radushkevich isotherm assumes that the characteristic of adsorption curve is related to the porous structure of the adsorbent and apparent energy of adsorption. This model is given by [23]:

$$q_e = q_s \exp(-B\varepsilon^2) \qquad (14)$$

where ε is the Polanyi potential equal to RT ln (1 + $1/C_e$), B is related to the free energy of sorption and q_s is the Dubinin–Radushkevich (D–R) isotherm constant. The linearized form is

POLLUTANT	DUBININ– RADUSHKEVICH ISOTHERM			TEMKIN ADSORPTION ISOTHERM		
	E (KJ mol $^{-1}$)	q_s (mg g $^{-1}$)	R^2	B (J mol $^{-1}$)	K_t (L g $^{-1}$)	R^2
Cefclidine	0.04524	6.447	0.9918	0.9170	12.03	0.9119
Cefepime	0.04489	5.317	0.9916	0.8466	10.32	0.9999
Cefluprenam	0.04390	7.281	0.9928	0.9357	15.82	0.9132
Cefoselis	0.04710	169.7	0.9973	1.0061	19.24	0.9338
Cefozopran	0.04430	33.48	0.9929	0.7899	9.042	0.9266
Cefpirome	0.04301	4.469	0.9959	0.7806	7.957	0.9397
Cefquinome	0.04321	4.749	0.9934	0.8089	8.312	0.9299

Table 4 Dubinin– Radushkevich Isotherm and Temkin adsorption isotherm for 4th generation antibiotics at temperature 303K and pH 7

$$\ln q_e = \ln q_s - 2BRT \ln\left(1 + \frac{1}{C_e}\right) \qquad (15)$$

The constant B gives the mean free energy of adsorption per molecule of the adsorbate when it is transferred from the solid from infinity in the solution and the relation is given as

$$E = \frac{1}{\sqrt{2B}} \qquad (16)$$

The D–R model, which does not assume a homogeneous surface or a constant adsorption potential as the Langmuir model, was also used to test the experimental data. It was applied to distinguish between physical and chemical adsorption of 4th generation antibiotics. The plots between ln q_e vs. ln (1+1/C_e) gives a straight line at all concentrations as shown in Fig. 7. The values of constants q_e and B thus obtained are given in Table 4. The value of regression coefficient was much lower than those of the other two isotherms at all studied concentrations. Therefore, in all of the cases, the D–R equation represented the least fit to experimental data than the other isotherm equations. The constant B gives an idea of the mean sorption energy, E, which is defined as the free energy transfer of 1 mol of solute from infinity of the surface of the adsorbent and can be calculated using the relationship in eqn (14). If the magnitude of E is < 8, then it is physical adsorption; if it ranges from 8-16 it is chemical adsorption. Thus from the analysis, E value ranges between 0 and .05 in all 7 compounds, hence it is physical adsorption.

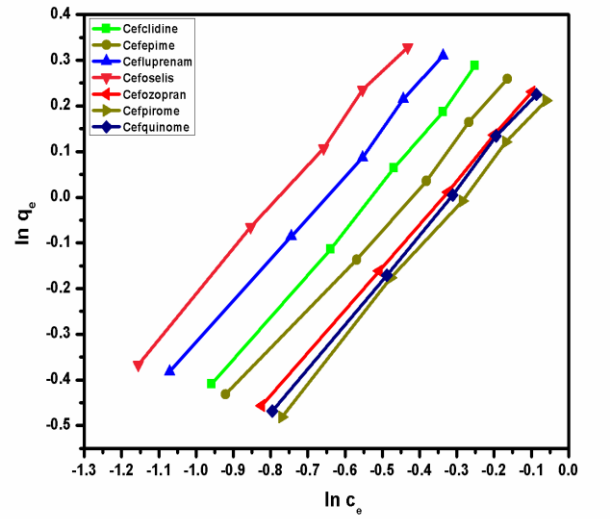


Fig. 6 A Freundlich plot (ln q_e vs. ln C_e) for 4th generation antibiotics adsorption by graphene. Conditions: pH = 7.0; temperature = 303 K and concentration = 0.5-2.5 mg L $^{-1}$.

d. Temkin isotherm

Temkin is used for determining heat adsorption value and binding energy value. The linear form of the Temkin isotherm equation is represented by the following equation [24]:

$$q_e = B \ln K_t + B \ln C_e \qquad (17)$$

where B = RT/b, T is the absolute temperature in Kelvin, R the universal gas constant (8.314 J K^{-1} mol), 1/b is the

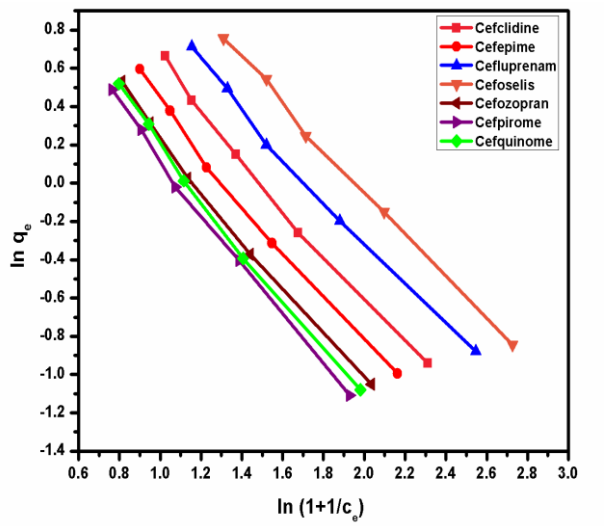


Fig. 7 A Dubinin-Radushkevich plot (ln q_e vs. ln 1+1/C_e) for 4th generation antibiotics adsorption by graphene. Conditions: pH = 7.0; temperature = 303 K and concentration = 0.5-2.5 mg L^{-1}.

Temkin constant related to the heat of sorption (kJ mol^{-1}) which indicates the adsorption potential (intensity) of the adsorbent, K_t the equilibrium binding constant, and the constant B is related to the heat of adsorption. Values of B and K_t were calculated from the plot of q_e vs. ln C_e as shown in Fig. 8. The values of B and K_t thus obtained are given in Table 4.

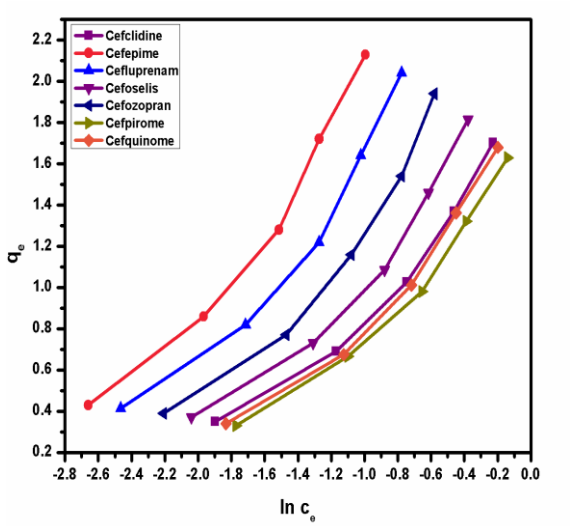


Fig. 8 A Temkin plot (q_e vs. ln C_e) for 4th generation antibiotics adsorption by graphene. Conditions: pH = 7.0; temperature = 303 K and concentration = 0.5-2.5 mg L^{-1}

F. Thermodynamic parameters

a. Adsorption kinetics at various temperatures

Using pseudo first and second order Lagergren equations (eqns. (2) & (5)), the rate constants are obtained at various temperatures (303, 313, 323, 333, 343 and 353 K) and at a constant concentration (2.5 mg L^{-1}). The plot between log (q_e-q_t) vs. t (1st order) and t/q_e vs. t (2nd order) will give a linear relationship from which k_1 and q_e; k_2 and 1/q_e are determined respectively using the slope and intercept.

The computed results are represented in Table 5. From first order, the results show that the theoretical q_e (cal) value doesn't agree with the experimental q_e (exp) values at all temperatures studied with a poor correlation co-efficient.

So, the experimental data were fitted further with a second order Lagergren model. From second order, the plots were found to be linear with good correlation coefficients as shown in Fig. 9. The theoretical q_e (cal) values agree well with the experimental q_e (exp) values. This implies that the second order model is in good agreement with the experimental data and can be used to favourably explain the 4th generation antibiotics adsorption on graphene at various temperatures.

Thermodynamic behaviour of 4th generation antibiotics on graphene was evaluated by the thermodynamic parameters viz., Gibbs free energy change (ΔG°), enthalpy (ΔH°), and entropy (ΔS°). These parameters were calculated using the following equations [16, 25]:

$$\ln K_2 = \ln C - \frac{E_a}{RT} \quad (18)$$

$$\ln K_c = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (19)$$

$$\ln K_c = \frac{\Delta S}{\Delta R} - \frac{\Delta H}{RT} \quad (20)$$

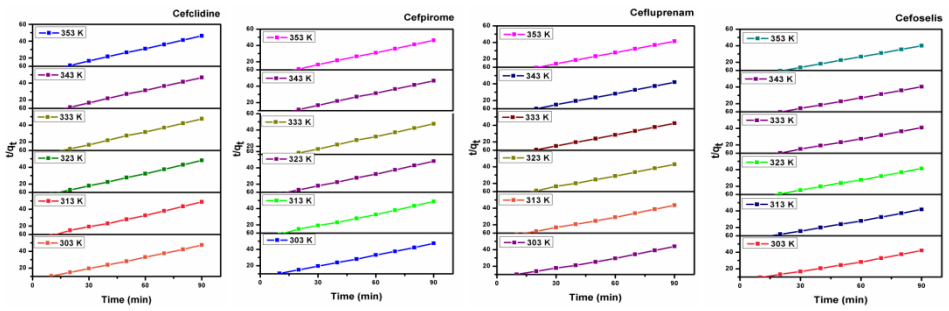
$$\Delta G = -RT \ln K_c \quad (21)$$

where C is the constant of equation (g mg min^{-1}), E is the energy of activation (J mol^{-1}), K_c is the equilibrium constant, R is the gas constant and T is the temperature in K. Fig. 10 shows that the rate constants vary with temperature according to eqn (17). The value of ln k_2 is obtained from the second order kinetics with varying temperature and with a constant concentration. The ln k_2 value is shown in Table 6. The activation energies E_a are calculated for 4th generation antibiotics from the slope of fitted equation. The ln K_c is obtained from eqn. (19) at various temperatures.

The enthalpy change (ΔH°) and entropy change (ΔS°) were obtained from the slope and intercept of the van't Hoff linear plots of ln K_c versus 1/T (Fig. 11) (eqn (20)). A positive value of enthalpy change (ΔH°) indicates that the adsorption process is endothermic in nature and the negative value of change in internal energy (ΔG°) shows the spontaneous adsorption of 4th generation of antibiotics on the adsorbent. Positive value of entropy (ΔS°) change shows the increased randomness of the solution interface during the adsorption of 4th generation antibiotics on the adsorbent (Table 6). The free energy change is obtained from eqn (21). The values of K_c and ΔG° are presented in Table 6. From

POLLUTANT	TEMPERATURE (K)	q_e (exp) (mg g^{-1})	FIRST ORDER KINETICS			SECOND ORDER KINETICS		
			q_e (Cal) (mg g^{-1})	K_1 (min^{-1})	R^2	q_e (Cal) (mg g^{-1})	K_2 (min.g mg^{-1})	R^2
Cefclidine	303	1.94	4.78	0.05587	0.3738	1.89	0.02840	0.9971
	313	1.99	3.98	0.05654	0.3473	1.98	0.04049	0.9975
	323	2.04	5.08	0.08259	0.4074	2.02	0.07404	0.9998
	333	2.09	10.02	0.12110	0.5742	2.07	0.11860	0.9898
	343	2.14	4.1	0.09126	0.5672	2.13	0.16040	0.9997
	353	2.19	3.53	0.08816	0.6621	2.19	0.20780	0.9995
Cefepime	303	1.81	3.58	0.05159	0.6621	1.81	0.0330	0.9994
	313	1.84	7.82	0.09099	0.5036	1.80	0.06096	0.9974
	323	1.86	8.79	0.10255	0.5045	1.854	0.08936	0.9994
	333	1.89	8.32	0.10868	0.4352	1.85	0.1333	0.9995
	343	1.91	6.01	0.02503	0.4182	1.90	0.1877	0.9996
	353	1.94	6.61	0.1093	0.3232	1.92	0.2288	0.9994
Cefluprenam	303	2.04	6.68	0.07176	0.3030	2.01	0.03465	0.9949
	313	2.06	11.93	0.10609	0.4727	2.02	0.05864	0.9982
	323	2.09	8.11	0.09961	0.5272	2.07	0.0976	0.9988
	333	2.11	10.8	0.12411	0.5334	2.10	0.1509	0.9998
	343	2.14	6.46	0.11271	0.5920	2.01	0.2475	0.9996
	353	2.17	7.98	0.13566	0.6082	2.16	0.3236	0.9999
Cefoselis	303	2.13	8.86	0.08302	0.4703	2.07	0.03415	0.9963
	313	2.15	20.4	0.12337	0.5313	2.12	0.05864	0.9987
	323	2.17	21.9	0.13233	0.5889	2.16	0.0976	0.9993
	333	2.20	21.6	0.14469	0.6233	2.17	0.15090	0.9998
	343	2.22	7.59	0.12155	0.5717	2.22	0.24750	0.9992
	353	2.25	9.42	0.1320	0.5992	2.24	0.32360	0.9999
Cefozopran	303	1.70	3.50	0.0576	0.4122	1.70	0.05401	0.9998
	313	1.72	3.75	0.0648	0.4851	1.726	0.07732	0.9985
	323	1.75	8.94	0.1046	0.5713	1.721	0.1081	0.9989
	333	1.77	5.11	0.0907	0.5596	1.77	0.1556	0.9996
	343	1.80	13.81	0.1357	0.5797	1.79	0.1989	0.9998
	353	1.82	14.05	0.1440	0.6055	1.81	0.2809	0.9998
Cefpirome	303	1.63	13.0	0.0991	0.4758	1.6	0.02467	0.9888
	313	1.65	11.8	0.1091	0.5214	1.61	0.06146	0.9969
	323	1.68	10.2	0.1157	0.5366	1.66	0.1253	0.9995
	333	1.70	9.31	0.1250	0.5951	1.7	0.2421	0.9998
	343	1.73	7.66	0.1318	0.6077	1.72	0.4172	0.9991
	353	1.75	7.10	0.1420	0.6420	1.75	0.6689	0.9999
Cefquinome	303	1.68	14.7	0.0961	0.4915	1.67	0.0162	0.9839
	313	1.70	13.9	0.1031	0.5242	1.64	0.0356	0.9960
	323	1.73	13.4	0.1076	0.5619	1.7	0.06263	0.9973
	333	1.75	11.5	0.1162	0.5926	1.72	0.12202	0.9982
	343	1.78	9.86	0.1215	0.6113	1.76	0.20481	0.9994
	353	1.80	8.86	0.1284	0.6031	1.80	0.2958	0.9997

Table 5 A comparisons between the experimental and calculated q_e values for different temperatures in first and second order adsorption kinetics of 4th generation antibiotics on graphene at various temperatures, concentration 2.5 mg/L and pH 7



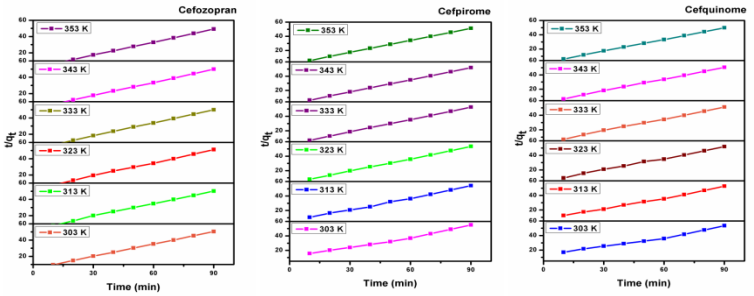


Fig. 9 Second order kinetic plot between different concentrations of 4th generation antibiotics for various temperatures vs. time. Conditions: pH= 7.0

POLLUTANT	TEMPERATURE (K)	K_c	ΔG° (KJ mol $^{-1}$)	ΔH° (KJ mol $^{-1}$)	ΔS° (J mol $^{-1}$ K)
Cefclidine	303 313 323 333 343 353	1.2146 1.6110 2.5198 3.8370 5.7013 8.2837	-0.4899 -1.2410 -2.4818 -3.7228 -4.9639 -6.2051	116.47	35.03
Cefepime	303 313 323 333 343 353	1.1853 1.5172 2.2436 3.2404 4.5801 6.3502	-0.4282 -1.0848 -2.1701 -3.2549 -4.3400 -5.4251	101.86	30.627
Ceftuprenam	303 313 323 333 343 353	1.1853 1.5172 2.2436 3.2404 4.5801 6.3502	-0.5993 -1.5181 -3.0513 -4.5545 -6.0726 -7.5909	142.49	42.841
Cefoselis	303 313 323 333 343 353	1.2685 1.7921 3.1186 5.1815 8.4101 13.283	-0.5292 -1.3406 -2.6813 -4.0221 -5.3629 -6.7037	125.87	37.846
Cefozopran	303 313 323 333 343 353	1.1617 1.444 2.0388 2.8193 3.8255 5.1018	-0.3776 -0.9563 -1.9129 -2.8695 -3.8260 -4.7825	89.79	27.001
Cefpirome	303 313 323 333 343 353	1.3528 2.0982 4.2038 8.0841 14.954 26.733	-0.7612 -1.9285 -3.8562 -5.7860 -7.7138 -9.6435	181.06	54.442
Cefquinome	303 313 323 333 343 353	1.3904 1.9371 3.6020 6.4527 11.174 18.755	-0.6791 -1.7206 -3.4413 -5.1619 -6.8828 -8.6034	161.61	48.593

Table 6 Thermodynamic parameters for adsorption of 4th generation antibiotics

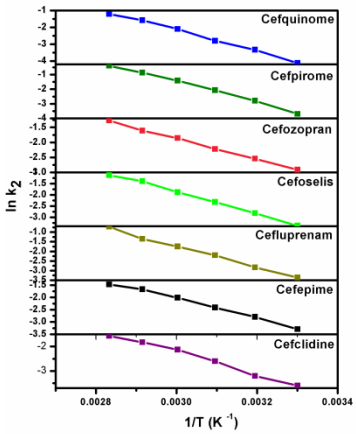


Fig. 10 Plot between ln k_2 vs. 1/T. Conditions: concentration: 2.5 mg L^{-1} and pH= 7.0.

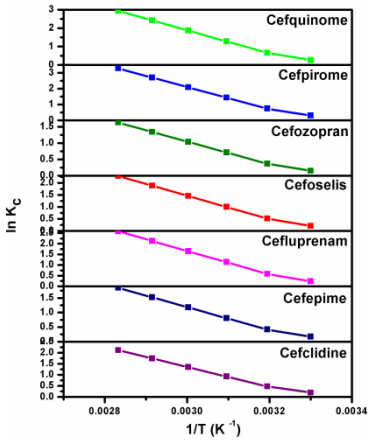


Fig. 11 Plot between ln K_c Vs 1/T. Conditions: concentration= 0.5 mg L^{-1} and pH= 7.0.

the table, it is found that the negative value of ΔG° indicates the spontaneous nature of adsorption.

I. CONCLUSION

The adsorption of Cefclidine, Cefepime, Cefoselis, Ceftuprenam, Cefozopran, Cefpirome and Cefquinome by high surface area graphene from aqueous solution was studied. This study shows that electrochemically exfoliated graphene is the most promising adsorbent which removes 4th generation antibiotic compounds effectively. The effect of different factors such as contact time, concentration, pH and temperature was studied. The adsorption capacity increases with increase in temperature indicating the endothermic nature of the adsorption process. The adsorption was studied kinetically and the experimental data were best fitted using the pseudo-second order kinetic model, which provided excellent correlation coefficients and agreement between the experimental adsorption capacities and the calculated one and it shows that the equilibrium is achieved within 60 min. The adsorption isotherm could be well fitted with Langmuir and Freundlich adsorption isotherm models. In D-R isotherm model, E value is < 8. Hence it indicates the process is physical adsorption. The thermodynamics study of the adsorption process showed the spontaneity of the adsorption since the ΔG° values were negative, the adsorption process was exothermic in nature with negative ΔH° values and the positive value of ΔS° shows the increased randomness of the solution interface during the adsorption of 4th generation antibiotics on the adsorbent.

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REFERENCES

[1] J.L. Santos, I. Aparicio, E. Alonso, A case study: Seville city Spain. Inter. 33, 2010, 596– 601.
[2] Yury Bayarski, Antibiotics: Types and Side effects, *eMed expert*, 2007
[3] "Drugs in water" Harvard letter, Harvard Health Publications, Harvard Medical School, 2011.
[4] Radjenovic´ a, M. Patriotic´ a, D. Barcelóa, Water Res. 43, 2009, 831–841.
[5] Y. Li, G. Zhu, W.J. Ng, S.K. Tan, Sci. Total Environ., 2009, 908–932.
[6] George Z. Kyzas, Jie Fu, Nikolaos K. Lazaridis, Dimitrios N. Bikiaris, Kostas A. Matis, Journal of Molecular Liquids, 2015, 87–93.
[7] Eckhard Worch, Adsorption technology in Water treatment-Fundamentals, Processes and Modelling, 2012, 1-302.
[8] Lateefa A. Al-Khateeb, Sitah Almotiry, Mohamad Abdel Salam, Chemical Engineering, Journal, 2014, 191-199.
[9] S. Wang, H. Sun, H.M. Ang, M.O. Tadé, Chemical Engineering Journal, 2013, 336–347.
[10] Yuan Zhuang, Fei Yu and Jie Ma, Journal of Nanomaterials, Article ID 675862, 2015, 1- 8.
[11] LÜ Meijiao, LI Jing, YANG Xuyu, ZHANG Changan, YANG Jia, HU Hao & WANG Xianbao, Chinese Science Bulletin, Vol.58, 2013, 2698-2710.
[12] Wei GAO, Graphite Oxide: Structure, Reduction and Applications, RICE UNIVERSITY, Texas, 2012, 1-133.
[13] George Z. Kyzas, Eleni A. Deliyanni and Kostas A. Matis, Society of Chemical Industry, 2013, 196-205.
[14] Subramanyan Vasudevan and Jothinathan Lakshmi, The adsorption of phosphate by graphene from aqueous solution, Royal Society of Chemistry,
[15] Pandian Ganesan, Ramakrishnan Kamaraj, Subramanyan Vasudevan, Journal of the Taiwan Institute of Chemical Engineers, 2013, 808-814.
[16] Jain Kassim, Tong Kim Suan, Rozaini Che Amat and Tan Lean Seey, Journal of Physical Science, Vol. 23(1), 2012, 1–13.
[17] Parimalam Ramachandran, Raj Vairamuthu and Sivakumar Ponnusamy ARPN Journal of Engineering and Applied Sciences, Vol. 6, no. 11, 2011, 15-26.
[18] Renugadevi, R. Sangeetha and P. Lalitha, Scholars Research Library Archives of Applied Science Research, 3 (3), 2011, 492-498.
[19] Indu Sharma and Dinesh Goyal, Journal of Scientific Research and industrial research, Vol. 66, 2009, 640- 646.

[20] Franklin L. burton, H. David Stensel, Wastewater engineering treatment and reuse, Metcalf & Eddy Tchobanoglous, 4th edition, 2003, 1138-1150.
[21] Langmuir I., The constitution and fundamental properties of solids and liquids, Journal American Chemical Society, 1916, 38: 2629.
[22] Taha M. Elmorsi1, Zeinhom H. Mohamed1, Walied Shopak1, Ahmed M. Ismaiel, Journal of Environmental Protection, 2014, 1667-168.
[23] Palanivel Sathishkumar, Mani Arulkumar, Veeramuthu Ashokkumar, Abdull Rahim Mohd Yusoff, Kumarasamy Murugesan, Thayumanavan Palvannan, Zainal Salam, Farid Nasir Anic and Tony Hadibarat, Royal Society of Chemistry, 2015, 30950-30962.
[24] P. Senthil Kumar, K. Kirthika, Journal of Engineering Science and Technology, School of Engineering, Taylor's University College Vol. 4, No. 4, 2009, 351 – 363.
[25] Muhammad Z Iqbalt and Ahmed A. Abdala, The Royal Society of Chemistry, 2013, 24455-24464.