RESEARCH ARTICLE

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Application of Experimental Design Methodology to Optimize Azithromycin Removal by Graphene/Iron Oxide Nanocomposite

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ABSTRACT: Currently, the occurrence and fate of antibiotics in the aquatic environment has become a very serious problem in that they can potentially and irreversibly damage the ecosystem and human health. For this reason, interest has increased in developing strategies to remove antibiotics from water. In this study, we report the several adsorption parameters including the adsorbent dosage, the initial azithromycin concentration, contact time, temperature, and pH were studied. The maximum adsorption Qmax. (9.89 mg g-1) was obtained after shaking the mixture for 30 min, at 298 K, and at neutral pH. The adsorption isotherm was analyzed by different isotherm models. The Langmuir and Freundlich isotherm models were found fitted to data well. The adsorption process follows second-order pseudo kinetics. The adsorption was endothermic (ΔH°= 39.64 kJ/mol), effective (ΔS° = 174 kJ/mol·K) and spontaneous (ΔG° = −15 KJ/mol). Overall, the findings in this study confirm that Graphene/Fe2O3 is a feasible and viable option for removing azithromycin from water in terms of water quality improvement and urgent antibiotics pollution control.

Keywords: Azithromycin dihydrate, Graphene/Fe2O3 nanocomposite, Kinetics, Thermodynamics parameters

INTRODUCTION

The presence of pharmaceutical and personal care products (PPCPs) in the receiving water has been reported to be an emerging and persistent risk for living beings. Emerging pollutants includes pharmaceuticals, pesticides, personal care products, hormones, detergent and food additives etc. (Abidi et al., 2019; Balarak et al., 2021a). Among PPCPs, β-lactam antibiotics such as Azithromycin (AZM) have been widely used to prevent the growth of bacteria by synthesizing their cell walls. These antibiotics, due to insufficient metabolism in the human body are excreted in significant amounts and enter the wastewater treatment plant. Antibiotics are a class of pharmaceuticals used against bacteria and other microbes (Cheng et al., 2020). They are classified into Penicillin, Cephalosporin, Aminoglycosides, Macrolides, Tetracycline and Fluoroquinolones (Abidi et al., 2020). They are extensively used and not fully metabolized and excreted through faces and urine. They are also continuously discharged to environment from hospitals and pharmaceutical industries and cause health problems like endocrine disrupting effects in aquatic organisms and produces antibiotics resistance in pathogens (Al-Mamun et al., 2019). Therefore, the rem Balarak et al. (2021b), report the adsorptive removal of azithromycin (AZM) antibiotics using activated porous carbon prepared from Azolla filiculoides (AF) (AFAC). The influence of the adsorption process variables, such as temperature, pH, time, and adsorbent dosage, is investigated and described. Rostamian and Behnejad (2016), study the adsorption properties of sulfamethoxazole (SMX) as an antibiotic were promoted by graphene nanosheet (GNS) and Graphene oxide nanosheet (GOS). The five factors influencing the adsorption of SMX (initial SMX concentration, initial solution pH, amount of adsorbent, temperature and contact time) were studied. Ehtesabi et al. (2019), study, a one-step hydrothermal reduction method applied for the preparation of 3D porous graphene hydrogel adsorbents. The characteristic properties of synthesized graphene hydrogels were obtained using scanning electron microscopy, Raman spectroscopy, Fourier transform infrared spectroscopy and Brunauer-Emmett Teller. Wahab et al. (2021), prepared, activated carbon (AC) and magnetic activated carbon (MAC) from Dalbergia sissoo sawdust for the removal of antibiotic Azithromycin (AZM) from aqueous solution. The effect of initial concentration, contact time, pH, adsorbent dosage, and the temperature were investigated for both the adsorbents. Cuerda-Correa et al. (2019), study the application of advanced oxidation processes (AOPs) for the removal of antibiotics from water has been reviewed. The present concern about water has been exposed, and the main problems derived from the presence of emerging pollutants have been analyzed. Photolysis processes, ozone-based AOPs including ozonation, O_3/UV, O_3/H_2O_2, and O_3/H_2O_2/UV, hydrogen peroxide-based methods (i.e., H_2O_2/UV, Fenton, Fenton-like, hetero-Fenton, and photo-Fenton), heterogeneous photo catalysis (TiO_2/UV and TiO_2/H_2O_2/UV systems), and sonochemical and electro oxidative AOPs have been reviewed. The main challenges and prospects of AOPs, as well as some recommendations for the improvement of AOPs aimed at the removal of antibiotics from

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wastewaters, are pointed out. Talaiekhozani et al. (2020), study the removal of azithromycin from water using ultraviolet radiation (UV), Fe (VI) oxidation process and ZnO nanoparticles. The effect of different parameters such as pH, temperature, hydraulic retention time (HRT), the concentration of Fe (VI) and ZnO nanoparticles and UV intensity on the removal of azithromycin from water was investigated. The optimal conditions for the removal of azithromycin were a pH of 2. Carabineiro et al. (2011), determined the adsorption capacity of ciprofloxacin (CPX) on three types of carbon-based materials: activated carbon (commercial sample), carbon nanotubes (commercial multi-walled carbon nanotubes) and carbon xerogel (prepared by the resorcinol/formaldehyde approach at pH 6.0).

Different techniques have been used for the removal of antibiotics from water. They include membrane filtration, electrochemical methods, degradation, adsorption method, ion exchange, solvent extraction and reverse osmosis etc (Behnajady et al., 2006; Bian et al., 2019). Adsorption is an efficient technique due to its cost effectiveness, simple in operation and no production of secondary pollution (Çağlar Yılmaz et al., 2020). Various adsorbents such as graphene, carbon nanotubes, activated carbon, Metal-Organic Frameworks (MOF) and chitosan have been used to remove antibiotics from water (Deng et al., 2015).

The researchers are trying to explore an efficient, nontoxic, selective and cost-effective adsorbent for the removal of antibiotics from water.

The composite of graphene/Fe_2O_3 is a good adsorbent with the specific characteristics for the elimination of antibiotics from water. The structure of graphene is two dimensional in which carbon atoms has sp^2 hybridization packed in a hexagonal lattice like honey comb. It has high adsorption capacity due to its large surface area (Çalışkan Salihi et al., 2021). The presence of Fe_2O_3 nanoparticles on the surface of graphene can avoid the agglomeration of graphene sheets and maintain its high surface area. Graphene/ Fe_2O_3 composite can be prepared by various methods like sol-gel method, hydrothermal method and microwaves method (Xu et al., 2013; Lyubutin et al., 2018).

METHODS AND RESULTS

Chemicals and Reagents

The chemicals such as Ethanol (C2H5OH), Iron oxide (Fe2O3), sodium hydroxide (NaOH), graphene and hydrochloric acid (HCl) manufactured by Sigma Aldrich were used in this study without any pretreatment.

Apparatus/Instruments

In this study Sonicater (power sonic 405), pH meter (pH7110), Electronic Balance (Shimadtzu X200), wrist Action Shaker (Model 75), hot plate (MSH 20A), Water bath, UV-Vis spectrophotometer (UVD-2960 Labomed. Inc.), etc. were used.

Adsorbent

The adsorbent Graphene/Iron oxide composite was prepared by solvothermal method. In this method 0.33 mg/mL of Fe2O3 dispersed in 300 mL ethanol. The solution was sonicated for 40 minutes in power sonic 405. Similarly, 2.5 mg/mL of graphene were dispersed in ethanol. Then after sonication 300 mL of Fe2O3 solution was added carefully drop by drop to the 200 mL dispersion solution of graphene. The prepared mixture was then placed in water bath to evaporate the ethanol. After that the solid mass of graphene/Iron oxide composite obtained. It was dried at 70 ºC temperature in oven for four hours.

Adsorbate

The adsorbent was used for the adsorption of Azithromycin antibiotic in this study. Azithromycin dihydrate is a white crystalline powder with a molecular formula of $C_{38}H_{72}N_2O_{12}.{}_2H_2O$ and a molecular weight of 785.0. Figure (1).

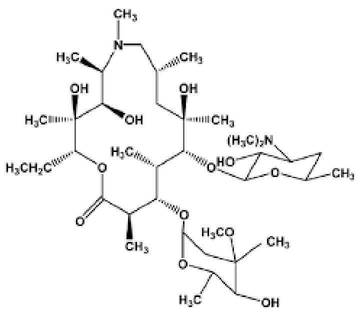

Figure 1. *Chemical structure of Azithromycin dihydrate*

Procedure

Preparation of Stock Solution of Adsorbate

In this study, 1000 ppm stock solution of adsorbate was prepared by dissolving 0.5 g of different Azithromycin dihydrate in distilled water in a 500 mL volumetric flask. The flask was filled up to the mark by adding more water. The stock solution was stored and diluted by dilution formula (C1V2 = C2V2) to the required concentrations when required.

Investigation of maximum absorbance (λ max.)

To investigate the maximum absorbance wavelength (λ_{max}.) of adsorbate various concentration of Azithromycin dihydrate were examine in UV-Visible range (200-800 nm) by using UV-Visible spectrophotometer (UVD-2960 Labomed. Inc). The maximum absorbance wavelength (λ max) measured for Azithromycin dihydrate was 236 nm. These values of λ_{max}. of Azithromycin dihydrate was used in the rest of experimental adsorption studies (Ibrahim et al., 2017).

Working or Calibration curve

The calibration curve for Azithromycin dihydrate was determined by plotting different concentration solution of Azithromycin dihydrate versus absorbance. The absorbance was investigated by using UV-Visible spectrophotometer. The calibration curve for the Azithromycin dihydrate is shown in the Figures 2.

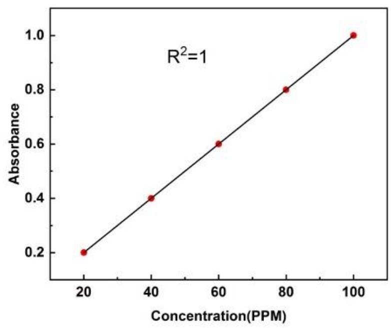

Figure 2. *Calibration Curve of Adsorption of Azithromycin onto Graphene/Fe2O3 nanocomposite*

Preparation of different pH solutions

The different pH solutions ranges from pH 1 to pH 7 were prepared in this study. The pH of solutions was adjusted by using 0.1 M hydrochloric acid (HCl) and 0.1 M sodium hydroxide (NaOH) solutions. The pH of solution was determined and adjusted by using pH paper and pH meter. Distilled water having pH 7 was considered as neutral solution.

By plotting absorbance versus concentration of antibiotics a linear regression equation was obtained from which the antibiotics concentration in the solution was calculated. The percent adsorption and equilibrium adsorption of antibiotics was calculated by applying the following equations.

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

$$Qe = C_o - C_e \times \frac{V}{m} \quad (2)$$

Where, Q_e is the equilibrium concentration of adsorbate (antibiotics) (mg/g), C_0 is the initial concentration (mg/L), Ce represents the final concentration and V show the volume of solution in (L) and m is mass of adsorbent in (g) respectively.

Batch Mode Adsorption study

In this research work the adsorption of antibiotic Azithromycin Dihydrate on graphene/Iron oxide composite was investigated by batch mode adsorption process. The conditions which affect the adsorption process such as pH, adsorbent does, contact time, concentration of antibiotics and temperature were investigated. To understand the mechanism of adsorption, various kinetic equations and isotherm models were applied. Thermodynamics parameters were also calculated from experimental data.

Influence of pH on adsorption of antibiotics

Adsorption process is very sensitive to the pH of medium. The pH of medium could change the surface charge of both adsorbate and adsorbent which affect the electrostatic force of attraction between them (Kadirvelu et al., 2005). The influence of pH on adsorption of antibiotic was studied at pH range from (1-7). The initial concentration of antibiotics was 50 ppm, adsorbent weight 0.005 g and shaking time 60 minutes. The maximum adsorption of Azithromycin dihydrate was at pH 7. The results are given in Figure 3. The graphene/Iron oxide nanocomposite used for removal of antibiotics contained different surface functional groups that show variable behavior by changing pH of the solution. The maximum adsorption of Azithromycin dihydrate was investigated at pH 6-7. The surface of Azithromycin dihydrate positive charge at pH < 3.0 and electrostatic repulsion decreases adsorption (Nigam et al., 2000). When pH increases from 3 to 6 the surface of Azithromycin dihydrate become negative charge can easily bind with positive charge adsorbent. At pH 7 the Azithromycin dihydrate exists in zwitterion and show maximum adsorption.

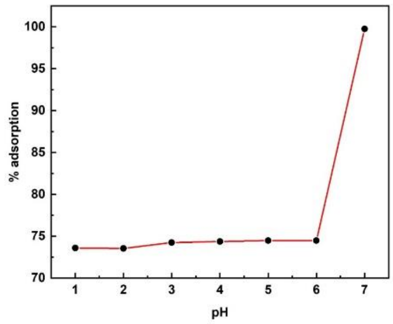

Figure 3. *The pH effect on adsorption of Azithromycin dihydrate by graphene/Iron oxide nanocomposite*

Effect of antibiotic concentration on adsorption

To explore the effect of initial concentration of the antibiotic adsorption on graphene/Fe_2O_3 composite were studied in range from (20 ppm to 160 ppm). The experiment was performed under optimized conditions. From the experimental results it was investigated that the adsorption efficiency of adsorbent increase with increase in concentration of antibiotics as shown in Figure 4. The increase in percent adsorption with increase in concentration of antibiotic was due to the available active sites on the surface of graphene/Fe_2O_3 composite (adsorbent).

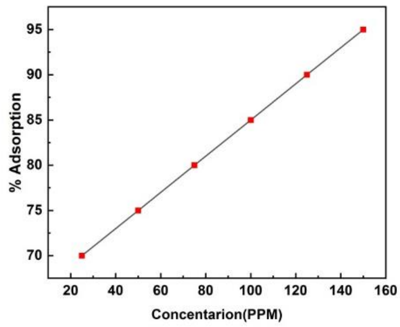

Figure 4. *The Concentration effect on adsorption of Azithromycin dihydrate by graphene/Iron oxide nanocomposite*

Various adsorption isotherms were applied to experimental data to understand the mechanism of adsorption. Freundlich model was used in the liner form as given bellow.

$$\log q_e = \log K_F + 1/n \log C_e \qquad (3)$$

Where q_e is amount of adsorbate (antibiotics) adsorbed at equilibrium, Ce represents adsorbate concentration at equilibrium. K_F and 1/n are Freundlich constants which show adsorption efficiency and adsorption intensity respectively. The values of K_F and

The pH had the highest effect on Azithromycin removal

1/n were calculated from slop and intercept by plotting qe versus Ce. The experimental results obtained from Freundlich adsorption isotherm (Figure 5). This indicates that adsorption data agreed well with Freundlich isotherm model (Ng et al., 2002; Majd et al., 2021). The values of Freundlich isotherm constants K_F and 1/n for Azithromycin dihydrate is given in Tables 1.

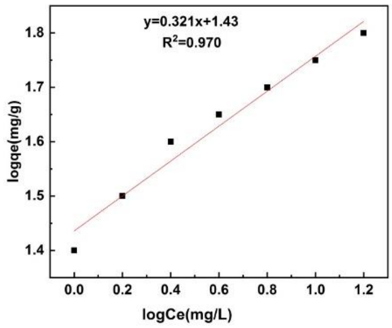

Figure 5. *Freundlich adsorption isotherms for azithromycin Dihydrate adsorption onto graphene/Fe2O3 nanocomposite*

The experimental date was subjected to Langmuir isotherm model (Langmuir et al., 1918). According to this model the adsorption of adsorbate occur at specific homogeneous active sites on surface of adsorbate. The following linear form of Langmuir equation was applied to experimental data.

$$\frac{C_e}{q_e} = \frac{1}{Q_{\max}} C_e + \frac{1}{K_L Q_{\max}} \qquad (4)$$

Here, Q_{max} represents maximum adsorption capacity, qe represent the amount of adsorbate adsorbed on adsorbent, Ce show equilibrium concentration of adsorbate in solution and K_L is Langmuir equilibrium constant (Ahmadi et al., 2013). The values of Q_{max} and K_L were determined from slop in the form of graphs. The values of Langmuir constants K_L and Q_{max} are given in Table 1. The value of dimensionless constant R_L of Langmuir isotherm was calculated by equation below.

$$R_L = \frac{1}{1 + K_L C_i} \qquad (5)$$

Where C_i represents initial concentration of adsorbate (mg/g) and K_L is Langmuir constant

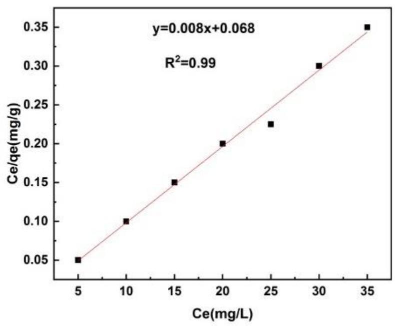

Figure 6. *Langmuir adsorption isotherms for azithromycin Dihydrate adsorption onto graphene/Fe2O3 nanocomposite*

Table 1. *The isotherm parameters of Azithromycin Dihydrate adsorption onto graphene/Fe2O3 nanocomposite*

Models	Parameters	Values
	K_F(mg/g)	21.23978
	1/n	0.32143
Freundlich	R^2	0.970
	Q_{max}(mg/g)	9.891197
	R_L(dm^3/mol)	6.03
	K_L(mg/g)	1.20
Langmuir	R^2	0.99

The pH had the highest effect on Azithromycin removal

Effect of the amount of adsorbent

Adsorption capacity of adsorbent is highly affected by changing the amount of adsorbent. The effect of the amount of adsorbent (graphene/Fe_2O_3) on the adsorption of antibiotics were studied at optimized pH and contact time in ranges from 0.001 to 0.015 g/10mL for azithromycin Dihydrate. The experimental results reveal that adsorption of antibiotic increases with increase in amount of adsorbent as shown in Figure 7. This is due to more availability of surface site of adsorbent for the attachment of adsorbate molecules (Hu et al., 2019). The optimum adsorption 98.71% for azithromycin Dihydrate was observed at 0.006 g of adsorbent.

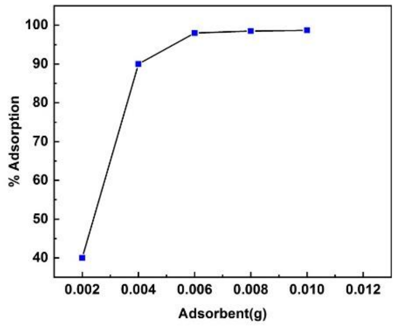

Figure 7. *Influence of adsorbent does on adsorption of Azithromycin Dihydrate by graphene /Fe2O3 nanocomposite*

Effect of shaking time

Shaking time has great effect the on adsorption process of antibiotic. The effect of shaking on adsorption of antibiotic by graphene /Iron oxide composite was investigated. The experiment was performed at shaking time from 10 to 60 minutes, adsorbent does (0.006 g), concentration of antibiotics 50 ppm, at optimum pH and room temperature. The adsorption of antibiotic was initially increased with increase in time. This because of the availability of more active sites on the surface of adsorbent at the beginning and then gradually saturation occurred. After equilibrium time no further increase in adsorption was observed (Mondal et al., 2007). The equilibrium time investigated for Azithromycin Dihydrate was 30 minutes. The experimental results are given in Figures 8, and this equilibrium shaking time was used for all experiments.

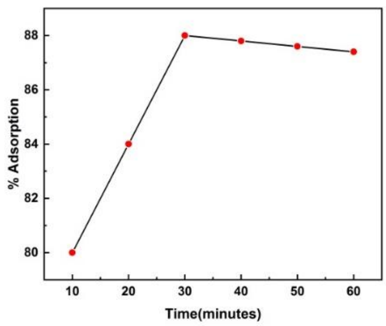

Figure 8. *Effect of shaking time on adsorption of Azithromycin Dihydrate by graphene /Fe2O3 nanocomposite*

Kinetic models were applied to understand the adsorption mechanism and rate of reaction.

The linear form of pseudo 2nd order equation was applied to experimental data as given bellow

$$t /q_t = t /q_e +1/ k_2 qe^2 \qquad (6)$$

Where qe^2 is concentration of antibiotics adsorbed at equilibrium, q_t concentration of antibiotics at time 't' and k_2 is rate constant for pseudo 2nd order equation. The graphs t /q_t versus t were obtained with correlation coefficient R^2 values (0.999) for Azithromycin Dihydrate. The graphs are shown in the Figure 9, which reveals that the experimental data agreed well with pseudo 2nd order kinetic model (Liu, 2008; Guo and Wang, 2019)

The pH had the highest effect on Azithromycin removal

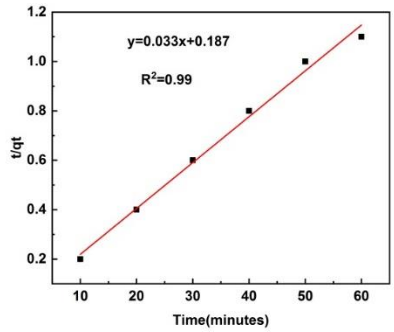

Figure 9. *Pseudo 2nd order kinetic model for Azithromycin Dihydrate onto graphene / Iron oxide nanocomposite*

To understand further the mechanism of adsorption Reichenberg equation was applied to experimental data. The Reichenberg (1953), equation explain that either intraparticle or film diffusion process is involved in the adsorption mechanism. The equation is given bellow

$$Q = (1 - \frac{6}{\pi^2})\, e^{-Bt} \qquad (7)$$

Where Q = qt/qe and Bt is a mathematical function of 'Q' which can be calculated from the following equation.

$$Bt = -0.4977 - \ln(1 - Q) \qquad (8)$$

The graphs obtained from the plot of 'Bt' versus 't' are shown in Figures 10. The linear line does not pass through origin which shows that initially intraparticle diffusion followed by film diffusion occurs between adsorbate (antibiotic) and adsorbent. The data are tabulated in Table 2.

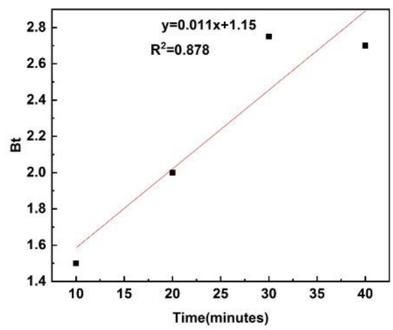

Figure 10. *Reichenberg model for Azithromycin Dihydrate onto graphene/Iron oxide nanocomposite*

Table 2. *Different kinetic parameters of adsorption of Azithromycin Dihydrate adsorption onto graphene/Fe2O3 nanocomposite*

	Azithromycin Dihydrate	
Models	Kinetic parameters	Values
	K_2 ($g/mg^{-1}min^{-1}$)	86475.47
Pseudo second order	R^2	0.99
Reichenberg	R^2	0.878

Effect of temperature on the adsorption of antibiotic onto graphene/Fe2O3 Nano composite

Adsorption process is highly affected by change in temperature. The influence of temperature on adsorption of antibiotic Azithromycin Dihydrate was studied in the temperature range (298K to 318 K) at optimized conditions (Aksu et al., 2008). The experimental results indicate that adsorption of antibiotic on graphene/Fe_2O_3 composite decreases with increase in temperature as given in the Figure 11, show that adsorption process was exothermic in nature (Striolo et al., 2005).

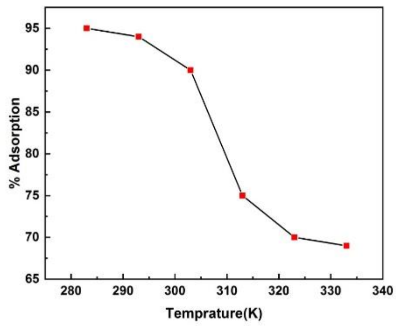

Figure 11. *Effect of temperature on adsorption of onto graphene/Fe2O3 nanocomposite*

Thermodynamic study

The different thermodynamic variables like enthalpy, entropy and Gibbs free energy were calculated with the help of the following equation.

$$\ln K_L = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (9)$$

$$\Delta G = \Delta H - T\Delta S \qquad (10)$$

$$\Delta G = - RT \ln K_L \qquad (11)$$

Where ΔS represent entropy (J/mol K), ΔH is enthalpy (kJ/mol) and ΔG is Gibbs free energy (kJ/mol), T show absolute temperature and R is gas constant (Motomura, 1978).

The value of K_L can be determined by the following equation

$$K_L = \frac{F}{1-F} \qquad (12)$$

The value of F show the fraction adsorbed at equilibrium. The values of ΔS and ΔH were calculated from the slop by plotting the value of lnKL verses 1/T and the results are given in Figure 12. The experimental results reveal that adsorption process was spontaneous, feasible and exothermic in nature (Pan et al., 2016). The thermodynamic parameters are given in Table 3.

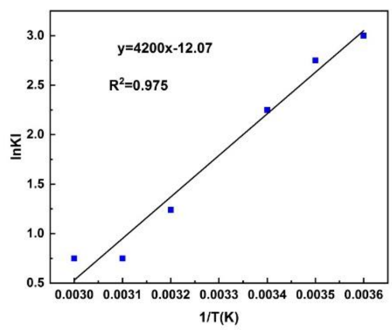

Figure 12. *Change in adsorption equilibrium of Azithromycin Dihydrate onto graphene/Fe2O3 nanocomposite with temperature.*

Table 3. *The thermodynamic parameters for the adsorption of Azithromycin Dihydrate onto Graphene/Iron Oxide nanocomposite*

Temperature	Δ**S**◦ kJ/mol·K	Δ**H**◦ kJ/mol·	ΔG◦ kJ/mol·
298	174.55	39.64	-12.39
308	174.55	39.64	-14.112
318	174.55	39.64	-15.857

CONCLUSIONS

The excessive use of antibiotics produces water pollution which leads to different environmental problems. Graphene/Fe_2O_3 composite was synthesized for the removal of antibiotics from water. The composite was used for the removal of Azithromycin dihydrate from aqueous solution. Various adsorption conditions which influence adsorption capacity of antibiotic on Graphene/Fe_2O_3 composite were optimized. The maximum adsorption capacity of Azithromycin dihydrate (98 %) at pH 7. To study the mechanism of adsorption different isotherm model and kinetic equations were applied to the adsorption data. Pseudo second order kinetic model agreed well with experimental results. The adsorption of Azithromycin dihydrate on adsorbent is fitted well to Freundlich and Langmuir models. The effect of temperature on the adsorption of antibiotic Graphene/Fe_2O_3 composite was studied and thermodynamic parameters such as ΔG, ΔS and ΔH were calculated. The results show that adsorption process is feasible, spontaneous and endothermic in nature.

CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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