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Original Article

EQUILIBRIUM, ISOTHERM, KINETIC AND THERMODYNAMIC ADSORPTION STUDIES OF TETRACYCLINE HYDROCHLORIDE ONTO COMMERCIAL GRADE GRANULAR ACTIVATED CARBON

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ABSTRACT

Objective: The work presented here reveals the adsorption pattern of Tetracycline Hydrochloride (TC-HCl) onto granular activated carbon (GAC) in a batch process.

Methods: Initially the consequence of various factors such as initial concentrations at various time intervals, pH (1- 7) and temperature (15, 28, 50 °C) were carried out.

Results: The removal efficiency increased with an increase in initial concentration from 200mg $L^{-1}$to 800mg $L^{-1}$and then decreased up to1000 mg L-1. The adsorption capacity was found to be maximum in the pH range of 6-7. The estimated enthalpy was -22.540 kJ mol^{-1}. The initial and treated GAC were characterized by SEM that elucidated the surface pattern of TC-HCl onto GAC. The scrutinization of kinetic studies revealed that Pseudo first order and Pseudo second order model gave an excellent fit with experimental data. Among the four equilibrium models, Freundlich and Temkin isotherm model gave a good fit and confirms that the adsorption behavior of TC-HCl onto GAC is controlled by chemisorption.

Conclusion: Thus, batch adsorption of TC-HCl onto GAC was controlled by chemical reaction and an exothermic process.

Keywords: Granular activated carbon (GAC), Tetracycline hydrochloride (TC-HCl), Adsorption, Isotherm, Kinetics, Thermodynamics, Batch process.

INTRODUCTION

The era of antibiotics started in the beginning of twentieth century before which the treatment was based on folklore medicines. The traditional way of curing diseases followed by many culture such as Indian, Chinese, Egyptians, Greeks, Arabs have used plants with antibiotic like properties and also molds in their treatment processess. For example, cinchona bark was used in the treatment of malaria in the 17th century itself. Antibiotics are one of the most widely used chemical compounds for treating several bacterial infections in organisms living on soil and water. They are used mostly to prevent infections rather than complete cure. Penicillin, the first antibiotic that was accidentally discovered by Alexander Fleming in 1928 saved many lives during the second world war between (1939-45). The major classes of antibiotic includes aminoglycosides, ketolides, macrolides, fluoroquinolones, β-lactams, lincosamides, glycopeptides, oxazo-lidinones, streptogramins, sulfonamides, tetracyclines etc., Antibiotics are ubiquitous compounds and its usage has been increasing day by day. Moreover, the steady increase of active pharmaceutical ingredients (API) in dosage forms and also the side chain modifications of these API has become a continuous process in order to treat against growing infections. Such modifications and alterations in antibiotics show that the resistance genes are also proliferating at the same rate.

Tetracycline comes under the class of broad-spectrum antibiotics discovered by Benjamin Duggar in the year 1945 and came to use from the year 1948. It is used against several bacterial infections in human, veterinary and also used for agricultural purposes. They are commonly used in the livestock farming. It is a broad spectrum antibiotic (active against several gram +ve and gram –ve bacteria, anerobic bacteria, protozoas), bacteriostatic they interfere with bacterial protein synthesis [1]. The physical properties of tetracycline hydrochloride (TC-HCl) are as follows, it is a yellow crystalline drug, the hydrochlorides of tetracycline's are highly soluble in water with a half-life of 6 to 12 hours; the bioavailability is 100% if taken via intravenous route and about 50% if taken via oral route and 50-80% [2] of tetracycline gets excreted through feces and urine in an unchanged form from the system. For veterinary purposes, the dosage pattern depends on the body weight of the animal, (more the body weight ,more drug were administered to animals) simultaneously the consumption rate also varies from time to time.

Pharmaceutical pollution has drawn the attention of many researchers recently worldwide and considered them as one of the emerging pollutions though the amount detected in the environment is under permissible levels. Studies have proven that compounds of antibiotic origin are partially eliminated in wastewater treatment plants (WWTPs). Reuse of WWTPs may result in occurrence of antibiotic residues in soil, ground water, etc., [3].Other studies have shown that WWTPs are dominant sources of tetracycline residues as they cannot remove tetracycline completely [2]. Tetracycline's have been detected in soils, surface waters etc.,[4,5]. The polar compounds when discharged out directly comes into contact with the environmental biota, and they pave a way for developing resistance genes and this could be one of the possible reasons for the growing resistant genes against tetracycline as well as other polar pharmaceutical compounds in recent years. From a mariculture farm in China the tetracycline resistance genes *tetD, tetB* and *tetA* have been isolated [6]. Tetracycline's can persist for a longer period of time in the environment if sunlight is not present [7]. Among various antimicrobial agents tested 57% resistance rates were observed for tetracycline [8]. Thirty different tetracycline resistance genes have been characterized [9]. It is very crucial to understand the removal of tetracycline through an activated sludge process as it is difficult to predict mass load and risk assessment management [2]. Adsorption is a simple and effective treatment in the removal of pollutants, and especially activated carbons have been used widely in the removal of organic micro pollutants and have also attracted the researchers in the adsorption of pharmaceutical products as they do not produce any further metabolites [10]. Tetracycline adsorption has been studied extensively on soils, clays, to etc. Granular activated carbon are the most widely preferred ones for adsorbing a wide range of compounds in several industries, and they are a part of most of the effluent treatment plants (ETP) worldwide. Owing to the basic knowledge of tetracycline adsorption the intention of the presented work here was to study on the adsorption pattern of the TC-HCl onto commercial grade granular activated carbon in a batch process and to know about its type of adsorption and relationship between the adsorbate and adsorbent through isotherms, rate of adsorption through kinetics and heat of adsorption through thermodynamics. The results from the batch studies would be useful to carryout column studies that would be more applicable for continuous removal systems.

MATERIALS AND METHODS

The tetracycline hydrochloride [TC-HCl] was bought in the capsule form, as Resteclin 250 I. P, (Indian Pharmacopoeia) Abbott healthcare Pvt. Ltd., Chennai, India, that contains Tetracycline Hydrochloride I. P. Commercial grade granular activated carbon was bought from Sudhakar Biologicals, Chennai, India. The solution of TC-HCL was prepared using distilled water. The pH of the synthetic effluent was varied by the addition of 0.1 Please provide space 0.1N HCl/NaOH. The GAC was sieved for uniform size and the particles retained on +10/-8 mesh was taken for batch studies. Before carrying the batch studies, GAC was thoroughly washed with water. Around 10 cycles of water wash were provided to remove the particles that would have been adhered to the surface of GAC and three cycles of 0.1N concentrated HCl wash were given to activate the surface of by removing the air molecules from the pores of GAC.

Batch studies

Batch adsorption studies were carried out in 250 ml Erlenmeyer flasks containing 100 ml of TC-HCl solutions. At the outset experiments were carried out for an increasing initial concentrations (200-1000 mg L^{-1}) at a constant temperature of 28°C to find out the equilibrium time and saturation adsorption capacity. Furthermore the effects of pH (1.2, 2, 3, 4, 5, 6, 7) for an initial drug concentration of 800 mg L^{-1}were carried out. Subsequently by varying the temperature (15°C, 28°C and 50°C) experiments were carried out for an initial drug concentration of 800 mg L^{-1}at pH 6. All the experiments were carried out by adding 1g of GAC to the flasks containing the synthetic effluent and agitated at an unvarying speed of 200 rpm until an equilibrium point was reached.

Determination of TC-HCl

The concentration of TC-HCl in Resteclin capsules was measured spectrophotometrically [11] using double beam UV-VIS spectrophotometer (UV Pharmspec 1700, Shimadzu) at 360 nm [12]. The maximum peak was observed at 360 nm in the wavelength scan mode with an absorbance value of 0.451 and percentage transmittance of 39.57. The Beer's law is obeyed for the concentration range of 0.1 – 1 (mg/ml). The same method was followed to identify the concentration of TC-HCl at various experimental conditions.

SEM Analysis

The surface characterization of the adsorbent before and after adsorption was carried out using Scanning electron Microscopy(Hitachi S-3400 N). The analysis were carried out by placing a small amount of the adsorbent coated with a coating material and allowed to dry under mercury lamp for about 5-10 minutes and after drying the analysis were carried out.

Data Analysis

Uptake rate of TC-HCl

The uptake rate of TC-HCl was calculated using the following equation

$$q = V * (C_i - C_f)/m (1)$$

Where, q is the adsorption capacity (mg g^{-1}), V is the volume of the TC-HCl solution (ml), C_i is the initial concentration of the solution (mg L^{-1}), C_f is the final concentration (mg L^{-1}) of the solution and m is the mass of the adsorbent in (g).

Removal Efficiency of TC-HCl

The removal efficiency of TC-HCl from the solution was calculated using the following equation

$$Removal\ Efficiency\ (\%) = \frac{C_i - C_f}{C_i} * 100 \text{ ....(2)}$$

where, C_i is the initial concentration of the solution (mg L^{-1}), C_f is the final concentration (mg L^{-1}) of the solution.

Thermodynamic studies of adsorption process

The thermodynamic analysis of the batch adsorption of TC-HCl were evaluated at three different temperatures (15°C, 28°C and 50°C) for an initial adsorbate concentration of 800 mg L^{-1}. The standard Gibbs free energy was calculated using the following equation (3) [13,14].

$$\delta G = -RT \ln(K_{ad}) \text{ .... (3)}$$

where δG,is the change in Gibbs free energy (kJ mol^{-1}),R is the universal gas constant (8.314 J mol^{-1} K^{-1}),T is the temperature in degree celsius (°C) and K_{ad} is the apparent equilibrium constant that was calculated using equation (4)

$$K_{ad} = C_i/C_e \text{ .... (4)}$$

Using the thermodynamic relation of Gibbs free energy the enthalpy and entropy can be evaluated. From the basic laws of thermodynamics the relationship between Gibbs free energy, enthalpy and entropy was shown in equation (5)

$$\delta G = \delta H - T\delta S \text{ .... (5)}$$

where, δH is the change in enthalpy (kJ mol^{-1}) and δS is the change in entropy (kJ mol^{-1}).

The equation (5) was modified using the equation (3) which yields the following expression that was shown in equation (6)

$$\ln K_{ad} = \frac{\delta S}{R} - \frac{\delta H}{RT} \text{ .... (6)}$$

The linear plot of ln K_{ad} against 1/T gives the slope and intercept of enthalpy and entropy respectively. The spontaneity of the adsorption process [15] was understood from the values of Gibbs free energy. The negative value of change in Gibbs free energy δG was an indication of favourable adsorption.

Adsorption Kinetic Studies

The rate of adsorption and the rate constants can be verified through kinetic models. The kinetic studies were useful in the augmentation of adsorption towers. The rate constants were estimated using the following kinetic models such as simple first order kinetics, pseudo first order, pseudo second order models and Weber Morris diffusion model.

The Pseudo first order kinetics (Lagergren's model) and Pseudo second order kinetics (Ho-McKay model) are widely used adsorption reaction models [14] to understand the mechanism of adsorption . These two models contain almost all mechanism and used to determine the rate controlling step of the adsorption process.

Simple first order kinetics

The expression for the simple first order kinetics is shown in equation (7)

$$\ln (C_f/C_i) = - K_1 t \text{ .... (7)}$$

Where C_f and C_i are initial and final concentrations (mg L^{-1}), Kis the first order rate constant (min^{-1}). The reaction rate constant was estimated from the linear plot of -ln (C_f/C_i) against t.

Pseudo-1storder Kinetics (Lagergren's equation)

The integrated expression for the Pseudo first order kinetics equation is shown in equation (8) [13,16,17,18].

$$\ln(q_e - q_t) = \ln q_e - (K_{11} t/2.303) \text{ ....(8)}$$

Where q_e is the equilibrium adsorption capacity (mg g^{-1}),q_t is the adsorption capacity at time t, K_{11} is Pseudo first order rate constant (min^{-1}). The linear plot of ln (q_e-q_t) versus t gives the slope of –k_{11}/2.303 and an intercept of lnq_e.

Pseudo 2ndorder Kinetics

The integrated expression for Pseudo second order kinetics was shown in equation (9) and the same equation was rearranged to equation (10) [13,18,19].

$$\frac{1}{q_e - q_t} = \frac{1}{q} + K_{12}\, t \ldots\ldots\ldots\ldots(9)$$

or

$$\frac{t}{q_t} = \frac{1}{K_{12}\, q_e^2} + \frac{1}{q_e} t \ldots\ldots\ldots\ldots(10)$$

Where K_{12} is the second order rate constant (g $mg^{-1}min^{-1}$), q_e and q_t are equilibrium adsorption capacity and adsorption capacity at regular time intervals. A plot of (t/q_e) versus t gives a slope of $(1/q_e)$ and intercept of $(1/K_{12}q_e^2)$

Weber Morris Model (1962)

The kinetic model of the diffusion mechanism is expressed by equation (11) [19]

$$q_e = R_{id}(\sqrt{t}) \ldots\ldots\ldots\ldots(11)$$

where R_{id} is the intraparticle diffusion rate constant mg $g^{-1}min^{-0.5}$. The plot of q_e against $\sqrt{t}$would provide the slope of diffusion rate constant.

The shifting of adsorbate onto the adsorbent involves a series of steps that includes

i) Diffusion of the solute from the solution on to the edge of the liquid film

ii) Transfer of solute from the edge into the surface of the adsorbent

iii) Diffusion from the surface into the pores of the adsorbent

iv) Uptake of absorbent through several mechanisms such as physical adsorption, chemical adsorption, ion exchange etc.,[17].

By considering the third step that offers intraparticle mass transfer resistance as the rate limiting step the following diffusion mechanism proposed by Weber –Morris was considered.

Equilibrium Studies: Adsorption Isotherms

The process of adsorption was studied dynamically by plotting graphs for constant temperature known as isotherms. These isotherms predict the behaviour of adsorption process. They can approximately tell the pattern of adsorption process. Different types of adsorption isotherms have been proposed namely Langmuir, Freundlich, BET etc.,[20].

The process of adsorption varies with parameters like time, temperature, pH, concentration etc., so the isotherms become unique for each and every process and becomes necessary to study these isotherms in order to understand the behaviour of the adsorbate-adsorbent relationship. The experimental data were fitted to two parameter [20] adsorption isotherms namely Langmuir, Freundlich, Temkin and Dubinin Raduskevich Models.

Langmuir Isotherm Model

This model explains the monolayer adsorption pattern of the adsorbate onto the adsorbent. It is generally applicable for homogenous surface [21,22,23,28,29]. The general form of the expression is given by equation (12) [28,29]

$$q_e = Q_L \frac{K_L C_e}{1+K_L C_e} \ldots\ldots\ldots\ldots(12)$$

The linear form of the Langmuir's expression was shown in equation (13)

$$\frac{C_e}{q_e} = \frac{1}{Q_L K_L} + \frac{C_e}{Q_L} \ldots\ldots\ldots\ldots(13)$$

Where, $\mathbf{C_e}$was the equilibrium concentration (mg L^{-1}), Q_L (mg g^{-1}) and K_L (L g^{-1})are the Langmuir's constants. A linear plot of C_e/q_e versus C_e gives the slope of $1/Q_L$ andintercept of $1/Q_LK_L$ respectively.

The special characteristic of Langmuir was expressed using a dimensionless constant R_L which was calculated using the following equation (14)

$$R_L = \frac{1}{1+C_i K_L} \ldots\ldots\ldots\ldots(14)$$

Where, C_i was the initial concentration. The kind of the adsorption were predicted from the R_L values [24] for an unfavourable condition $R_L > 1$, linear $R_L = 1$, favourable $0 < R_L < 1$,irreversible $R_L = 0$.

Freundlich Isotherm Model

This model explains the adsorption process for an heterogeneous surface [26]. The proposed Freundlich kinetic expression is given by equation (15) [25, 26]

$$\mathbf{q_e} = K_f C_e^{(1/n)} \ldots\ldots\ldots\ldots(15)$$

Where, K_f (mgg^{-1}) and n are Freundlich constants. Taking natural log on both sides the linear form of Freundlich equation is shown in equation (16) [25]

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \ldots\ldots\ldots\ldots(16)$$

The coefficients can be estimated from the slopes and intercepts of the plot. The value of the slope lies between 0 and 1 which is a measure of surface heterogeneity [20].

If the value of 1/n = 1 Partition between the 2 phases is independent,1/n > 1 Cooperative adsorption, 1/n < 1 Normal adsorption, 1<n<10 Favorable adsorption process.

Temkin Isotherm Model

This model is based on the adsorbent-adsorbate interaction [26] by omitting the extremely low and large values of concentration. The heat of adsorption should increase linearly with the coverage of the adsorption sites [28].

The expression of the Temkin's model is shown in equation (17) [26, 29]

$$q_e = B(\ln(aC_e)) \ldots\ldots\ldots\ldots(17)$$

Where, B is the Temkin's isotherm constant which is expressed in equation (18)

$$B = \frac{RT}{b}, \ldots\ldots\ldots\ldots(18)$$

The linearized form of the Temkin's expression is given in equation (19) [26]

$$q_e = B \ln a + B \ln C_e \ldots\ldots\ldots\ldots(19)$$

Where, B Temkins Isotherm constant, a Temkins isotherm equilibrium constant (L g-1), b constant related to heat of adsorption (kJ mol-1).

Dubinin–Radushkevich Isotherm Model

The Dubinin–Radushkevich model is used to predict whether the adsorption is physisorption or chemisorptions[28] by calculating the activation energy E. From the model the saturation capacity can also be calculated. The general and linearized form of Dubinin-Radushkevich model is shown in equation (20 and 21) [29].

$$q_e = Q_{DR} \exp(-\beta\varepsilon^2) \ldots\ldots\ldots\ldots(20)$$

$$\ln q_e = \ln Q_{DR} - \beta\varepsilon^2 \ldots\ldots\ldots\ldots(21)$$

Where, $\mathbf{Q_{DR}}$ is the saturation adsorption capacity (mg g^{-1}), βconstant mean free energy of adsorption per mole of adsorbate (mol^2J^{-2}), ε Polanyi potential that is calculated using the equation (22).

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \ldots\ldots\ldots\ldots(22)$$

Where, R is the universal gas constant (8.314 J mol^{-1} K^{-1}),T is the temperature in Kelvin (K) and E the mean adsorption energy that is calculated using equation (23)

$$\mathbf{E} = \frac{\mathbf{1}}{\sqrt{\mathbf{2\beta}}} \text{..............................} (23)$$

If the activation energy E < 8 kJ mol^{-1} the adsorption process is physisorption and if E is in between (8 -16 kJ mol^{-1}), the process is chemisorption in nature [28].

RESULTS AND DISCUSSION

Effect of pH

As shown in Fig.1. for an initial drug concentration of 800 mg $L^{-1}$and pH (1.5,3,4,5,6,7) the adsorption capacity was 10,15,22,43,65 and 64.5 mg g^{-1} respectively. As seen from the results it was obvious that increase in pH resulted in the increase of adsorption capacity. Moreover the TC-HCl solutions were unstable above pH 8 and this was observed within 48 hours of time and below pH 3 the TC-HCl solution was highly stable for more than three weeks as observed. As known that pH is a most significant factor it actually has got a considerable role in the adsorption process of tetracycline hydrochloride.

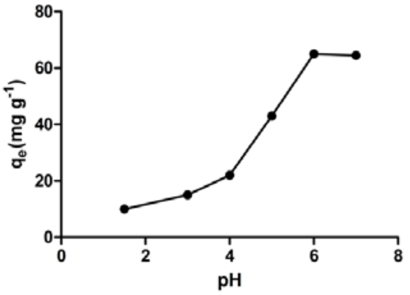

Fig. 1: Effect of pH on adsorption capacity.

The surface area of granular activated carbon is typically non polar electrically neutral and at normal conditions these compounds easily escape the adsorption process, greater the polarity greater will be the detachment from GAC. Tetracycline hydrochloride being an amphoteric molecule contains three ionizable groups and undergoes protonation and deprotonation reactions in aqueous solution[30]. Below pH 5 the TC-HCl molecule exists as a polar compound and interacts with π-electron donar on the carbon region and get repulsed, and the poor adsorption is due to planar geometry of tetracycline hydrochloride that undergoes van der waals interaction on GAC. In the pH range 6-7 the amino group of tetracycline hydrochloride facilitates cation-π bonding on the surface of the GAC and greatly adsorbed.

Effect of TC-HCl initial concentration

The TC-HCl removal onto GAC for different initial concentrations (200-1000 mg L^{-1}) was calculated using equation 2. From the results it was more clear that there was a noticeable change in the removal of TC-HCl with increasing concentrations. The removal efficiency was 68.6% for 200 mg L^{-1},83.61%, for 400 mg L^{-1}, 88.47% for 600 mg L^{-1}, 80.14% for 800 mg $L^{-1}$and 65.01% for 1000 mg L^{-1}. There was an increase in the removal efficiency for a concentration upto 600 mg $L^{-1}$and decreased further upto 1000 mg L^{-1}. From the results it was evident that change in concentration of TC-HCl solution changes the interaction rate between the adsorbate and adsorbent at the surface. There was more space for them to interact when the initial TC-HCl concentration was low to moderate and hence the removal efficiency was comparatively high at low and moderate concentrations of TC-HCl solution than at higher concentrations, though the number of active sites remained constant. The adsorption capacity was increased more or less at the same rate and saturation adsorption capacity was more or less analogous to all different concentrations.

Effect of contact time

The effect of contact time with respective to adsorption capacity was shown in Fig.2. for different concentration ranging from 200 -1000 mg L^{-1}. As the contact time was increased there was a gradual increase in the adsorption rate and showed a perfect relationship between the adsorbent and the adsorbate. For the chosen concentrations adsorption rate was increased for an increase in time and concentration and the heave of adsorption rate was in the increasing order of increasing concentration range. The saturation adsorption capacity was reached in the time interval of 150 – 200 minutes for different concentrations. The reaction rate was rapid within the first 60 min and later on the rate was decreased considerably and reached equilibrium around 200 min. The experiments were stretched for more than 300 minutes but no change was seen in the adsorption rate so the equilibrium time was predicted to be 200 minutes.

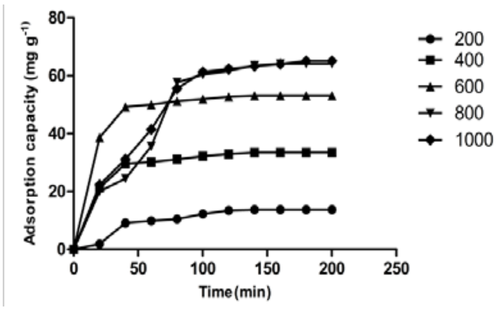

Fig. 2: Effect of time on different concentration of TC-HCl in mg L^{-1}

Effect of temperature

The effect of temperature on adsorption capacity was shown in Fig. 3. As seen from the Fig. 3. it was apparent that the temperature and adsorption capacity was directly proportional for the respective adsorbate- adsorbent association. The rate of adsorption decreased with increase in temperature. The uptake of TC-HCl on GAC was found to be 61.8,64.2 and 65 mg g^{-1} for 50, 28, 15°C. The adsorption rate was varied to some extent and decreased as the temperature was raised to 50°C. The decrease in adsorption capacity with respective to increasing temperature showed a linear pattern in the descending order of the adsorption rate. The possible damage of active sites [31] could be a reason for the decrease in the adsorption rate or when the temperature was increased the thickness of the boundary layer at the adsorbate surface might have decreased and this decrease in the boundary layer would have made the adsorbate to move back into the solution from the adsorbent surface easily [32]. Furthermore the increase in temperature resulted in the decrease of adsorption rate that suggested a weak interaction between the adsorbent surface and TC-HCl molecule and the type of adsorption process that supports such interaction is physisorption [32].

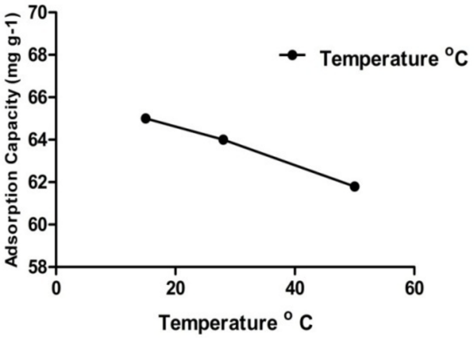

Fig. 3: Effect of temperature on adsorption capacity

Thermodynamic Studies

The value of change in Gibbs free energy δG was calculated using the equation [3] and the free energy for the adsorption process was found to be -6.908, -5.852, -4.961 kJ mol^{-1}) for the following temperatures (15, 28 and 50°C). The negative values of δG proved the spontaneity [33] of the adsorption process and from the results it was understood that higher the spontaneity of the adsorption process lesser the values of Gibbs free energy obtained. The dependency of the adsorption process on temperature can also be understood from the proximity of the δG values obtained,the δG values obtained for the temperatures 28 and 15 ^{o}C were closer to each other but for 50˚C the value obtained is higher than that of the other two temperatures. When the δG values were compared with the adsorption capacity it could be easily understood that as the temperature was increased the adsorption capacity was decreased. The closer the values of change in Gibbs free energy proves that adsorption process independent of temperature where it occurs. The plot of ln K_{ad} against 1/T was shown in Fig. 4. and from the slope and intercept the change in enthalpy and entropy was calculated. The nature of adsorption can be identified from the value of enthalpy calculated. If the value lies in the range of 2.1 -20.9 kJ mol^{-1}[33],its physisorption. The enthalpy value for the adsorption process of TC-HCl onto GAC was -22.540kJ mol^{-1} and thus the adsorption process can be characterized under chemisorption and exothermic by nature. The results obtained were in conformity with the experimental observations. The negative values indicate an energetically favourable adsorption process [15]. The change in entropy was calculated to be -54.712 kJ mol^{-1} K^{-1}. The negative value indicates decreased randomness at the interface of adsorbate and adsorbent. The negative value is strongly attributed to surface reaction rather than physical adsorption. The negative value of entropy was an indication of surface affinity of the adsorbent for TC-HCl molecules.

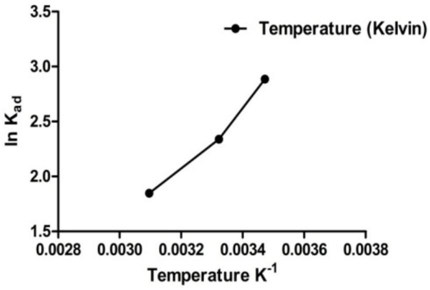

Fig. 4: Thermodynamic plot of Gibbs free energy

Adsorption kinetics studies

The simple first order kinetics shown in Fig. 5 gave a linear relationship with a poor regression coefficient. The equation gave a linear relationship of concentration against time, but since there was no complete exhaustion of TC-HCl from the solution onto the adsorbent the kinetic model proved to be invalid.

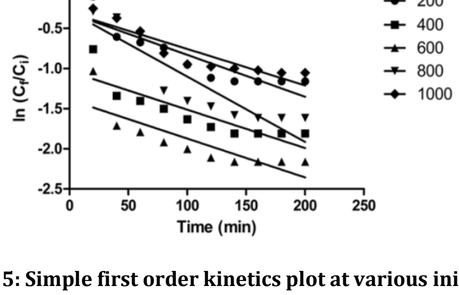

Fig. 5: Simple first order kinetics plot at various initial concentrations of TC-HCl in mg L^{-1}

From the linear plot of ln (q_e– q_t) against time shown in Fig.6. the slope and intercept were determined using which the values of rate constant K_{11} and q_e were estimated and the results were tabulated in (Table 1). Though there was a good correlation observed for this model through $R^{\wedge 2}$values obtained, the calculated adsorption capacity values did not match with experimental values. Moreover this model was valid only for initial period of time [34]and during the initial period, the adsorption would be rapid because of the availability of more active sites [35].

The equilibrium adsorption capacity values obtained theoretically were much greater than the values obtained experimentally. There was an increase in the adsorption rate obtained theoretically. There was an impact with the difference in increasing initial concentration that showed an increase in adsorption capacity both experimentally and theoretically for high initial concentrations. The time required to attain equilibrium did not vary much with increase in initial concentration. The R^2 values were in the range of 0.87-0.97. The pseudo first order rate constant decreased with increase in initial concentration.

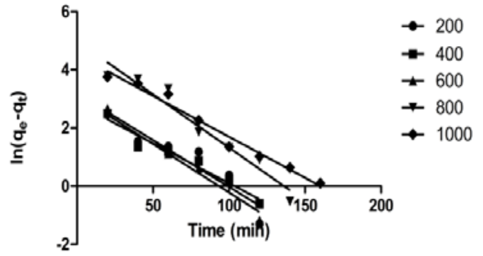

Fig. 6: Pseudo first order kinetics plot at various initial concentrations of TC-HCl in mg L^{-1}

From the linear plot of t/q_e against time shown in Fig.7. the slope gave equilibrium adsorption capacity and intercept gave the value of the second order rate constant. The suitability of this model was agreed from the corresponding correlation values. The estimated values were tabulated in (Table 1). From the results it could be seen that the $R^{\wedge 2}$values were in the range of 0.89-0.99 which proved that this model best fits the adsorption process. Moreover the equilibrium adsorption capacity estimated was almost closer to that of the calculated ones and this was the second possible reason to accept this model.

From the graph it could be seen that the lines were perfectly straight and there was some dissimilarity during the initial period of adsorption but towards the end of the equilibrium time the adsorption capacity did not vary a lot for all three concentrations at normal conditions. The graphical results were so apt with the experimental ones. The increase in the rate constant showed a decrease in the adsorption capacity for different concentrations. By considering all these factors it was suggested that Pseudo second order kinetics was highly convincing for the adsorption process. For longer period this model was more concrete compared to that of Pseudo first order kinetics that was valid only for initial period of time [36].

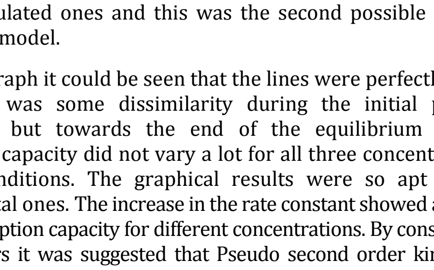

Fig. 7: Pseudo second order kinetics plot at various initial concentrations of TC-HCl in mg L^{-1}

According to the Weber Morris model (1962) the uptake rate varied proportionally with $\sqrt{t}$ and not directly with time. By considering the equation 11 in the form of y = mx a linear graph was plotted for q_e against $\sqrt{t}$ that produced a straight line and not a multi-linear line. Since the trend obtained was not straight the rate controlling mechanism was not through diffusion process however a multi-linear plot would conclude the involvement of two or more steps The intraparticle diffusion rate constants obtained were tabulated in table 1. It could be seen that as the concentration of TC-HCl increased the rate constants increased. Moreover the R^2 values obtained were in the range of 0.66-0.88 and thus this model could not be accepted. From this it was concluded that intraparticle mass transfer resistance was not the rate limiting step and thus the adsorption process of TC-HCl onto GAC might be speculated to have an ionic bonding interactions between them.

Equilibrium adsorption studies

The Langmuir isotherm model was chosen to know whether the adsorption process was appropriate to the characteristics of this model and moreover if the isotherm is found to be valid the maximum adsorption capacity corresponding to the total monolayer coverage on the surface of GAC can be estimated. The slope and intercept obtained from both linear and nonlinear equations, at three different temperatures, and the values of Langmuir constants Q_L and K_L were listed in Table 2. The R^2 values for linear model was in the range between 0.971-0.9867 and for nonlinear model it was in the range of0.8364-0.948. The values of Q_L shown in Table 2 was found to increase with decrease in temperature. It can be observed from the values obtained that certainly a good correlation was obtained with this model owing tothe adsorption capacity values obtained from the equations were above the experimental values and furthermore, the values of K_L that corresponds to the energy of adsorption [37] increased with increase in temperature. The separation factor R_L values were less than 0.1 and was found to show a favorable condition for adsorption process . For all the conditions provided the Langmuir's model was found to give a good fit for the experimental data. The adsorption type corresponding to Langmuir's model is physisorption, monolayer adsorption pattern and thus the type of adsorption process of TC-HCl onto GAC might follow a monolayer adsorption pattern. The linear and nonlinear curves of Langmuir plot is shown in fig. 8. It can be seen from the plot that the theoretical curves almost passes through the experimental points.

Table 1: Kinetic Parameters of Simple, Pseudo First order, Pseudo Second order and intraparticle diffusion models at 28°C for different concentrations

	Simple First Order Kinetics			Pseudo First order Kinetics				Pseudo Second order Kinetics			Intraparticle diffusion model	
At	C_i	K_1	R^2	q_{exp}	q_{cal}	K_{11}	R^2	q_{cal}	K_{12}	R^2	R_{id}	R^2
28^0C	200	0.0074	0.6256	13.72	24.23	0.07233	0.8749	16.71	0.001592	0.9871	1.152	0.678
	400	0.0048	0.7544	33.447	17.21	0.0632	0.9499	35.52	0.00266	0.9993	1.020	0.744
	600	0.0048	0.6894	53.08	21.67	0.06520	0.9468	55.06	0.00291	0.9996	0.888	0.683
	800	0.0081	0.8127	64.11	146.20	0.08428	0.9465	96.89	0.000124	0.8969	5.129	0.843
	1000	0.0045	0.8265	65.10	91.377	0.06489	0.9767	87.33	0.000198	0.9736	4.670	0.881

Table 2: Parameters of Langmuir adsorption isotherm model at different temperatures

	Linear Model				Nonlinear Model			
Temp °C	Q_L	K_L	R^2	R_L	Q_L	K_L	R^2	R_L
50	68.49	0.0704	0.9867	0.014	68.67	0.01459	0.948	0.0641
28	69.34	0.045	0.9860	0.021	73.19	0.03055	0.8968	0.0316
15	74.46	0.01945	0.977	0.0488	84.19	0.05056	0.8364	0.01939

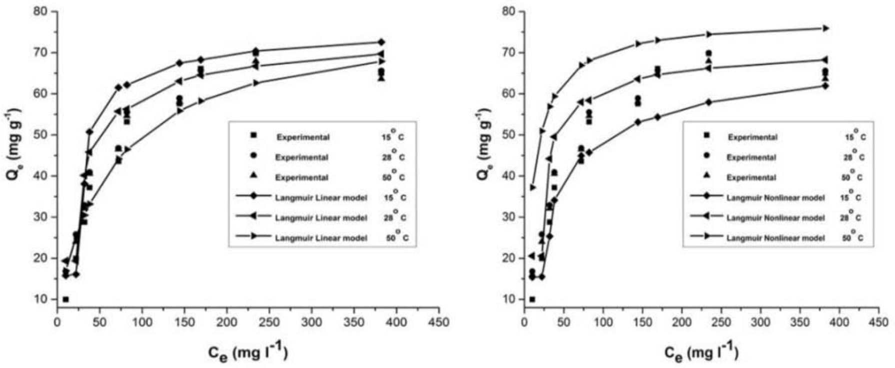

Fig. 8: Linear and Nonlinear plot of Langmuir adsorption isotherm model for TC-HCl adsorption onto GAC

The Freundlich isotherm model which provides an exponential distribution of active sights was chosen to study the suitability of the adsorption process of TC-HCl onto GAC.

The Freundlich constants K_f and n were calculated from the slope and intercept of the linear and nonlinear plot. The values of K_f, n and correlation coefficients were tabulated in (Table 3).

It can be seen from the Table 3 that R^2 values were in the range of (0.822-0.9192) for linear model and it was between (0.8529-0.896) for non linear model. The R^2 value was found to increase with decrease in temperature. The K_f values was found to increase with decrease in temperature for both linear and nonlinear models. The n value increased with increase in temperature. The value of 1/n calculated at three different temperature was less than 1 that corresponds to normal adsorption behaviour. The n value obtained at three different temperatures was in the range between (2.661-3.66) that corresponds to a favorable adsorption process of TC-HCl onto GAC. The results obtained were satisfactory with the given experimental data. This suggests that apart from homogenous adsorption behavior as concluded from Langmuir's model the availability of heterogeneous adsorption sites or possibilities of surface interaction (chemical interaction) between the adsorbate and adsorbent could be possible from the obtained results.

The experimental and predicted trend was shown in Fig.9.

Table 3 Parameters of Freundlich adsorption isotherm model at different temperatures

	Linear Model			**Nonlinear Model**		
Temp °C	**1/n**	**K_f**	**R^2**	**1/n**	**K_f**	**R^2**
50	0.3751	8.603	0.8221	0.4852	4.98	0.8529
28	0.3179	11.93	0.9113	0.3736	9.669	0.8864
15	0.2776	15.48	0.9192	0.2726	15.47	0.896

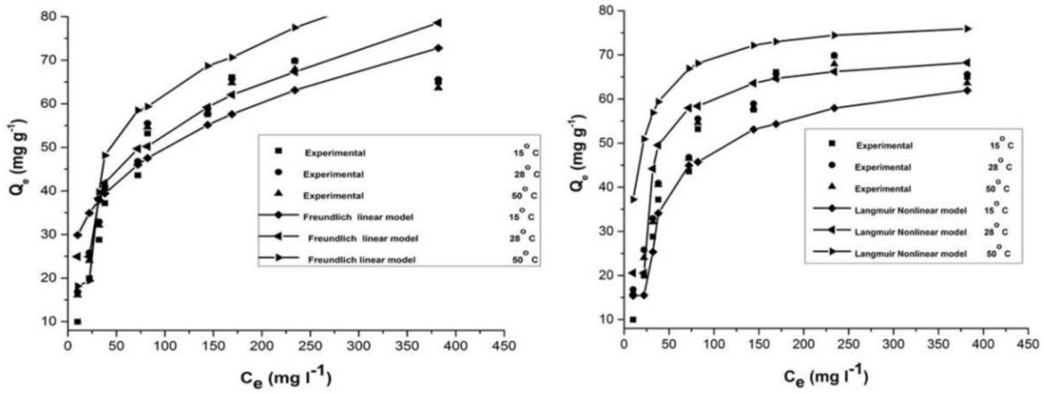

Fig. 9: Linear and Nonlinear plot of Freundlich adsorption isotherm model for TC-HCl adsorption onto GAC

Table 4 Parameters of Temkin adsorption isotherm model at different temperatures

	Linear Model			**Nonlinear Model**		
Temp °C	**a**	**b**	**R^2**	**a**	**b**	**R^2**
50	0.1758	0.155	0.9379	0.1674	0.153	0.9372
28	1.465	0.234	0.908	1.206	0.224	0.9061
15	17.88	0.324	0.8759	19.24	0.323	0.8747

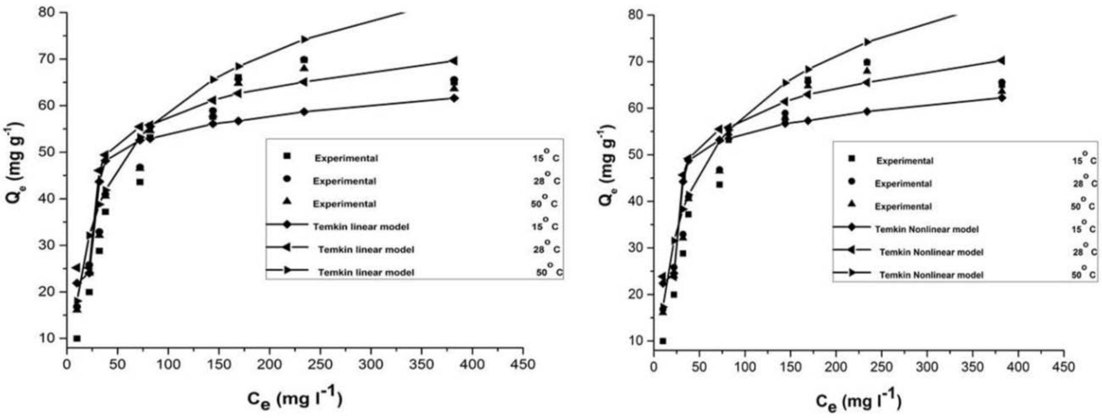

Fig. 10: Linear and Nonlinear plot of Temkin adsorption isotherm model for TC-HCl adsorption onto GAC

Temkin's model does not obey for extremely low and high concentrations [26]. The equation was derived based on certain assumptions like the adsorption sites were similar, owing to the impact of the substance adsorbed at the adjacent sites the energy of adsorption decreases directly with the increase in active site coverage, when all the active sites are used the distribution of energy is uniform along the length of the active site coverage and in addition to this the coverage neither approaches zero or unity. The Temkin's constant were obtained from the linear and nonlinear plot of the isotherm model. The estimated parameters of Temkin's model were listed in table 4 The value of heat of adsorption was found to decrease with increase in temperature as the adsorption sites were occupied. From the results it can been seen that the adsorption sites were occupied more at low temperatures than at higher temperatures. As this model explains the multivalent surface interactions of the adsorbate onto the surface of the adsorbent the high correlation values obtained shows that surface interactions between GAC and TC-HCl may possibly be the dominant process in the adsorption of TC-HCl on to the surface of GAC. The experimental and theoretical plots were shown in Fig.10.

The D-R model gave reasonably a good fit with accurate description of the data. The regression coefficient values (R^2) were less than 0.8. The activation energy was less than 8 (kJ mol^{-1}) that proved the adsorption type was physisorption. The D-R model also showed the temperature dependency [20] of the adsorption process, the activation energy E increased with decrease in temperature as shown in Table 5. The parameters of linear and nonlinear plot Q_e against $\boldsymbol{\varepsilon}^2$ were listed in Table 5.

The mean free energy of adsorption per mole of adsorbate decreased with decrease in temperature. The experimental and theoretical plots shows a poor fit with the respective model.

Table 5 Parameters of Dubinin –Radushkevich adsorption isotherm model at different temperatures

	Linear Model				Nonlinear Model			
Temp °C	**Q_{DR}**	**β**	**E**	**R^2**	**Q_{DR}**	**β**	**E**	**R^2**
50	53.30	0.01825	5.227	0.7491	50	0.0478	3.23	0.7803
28	53.51	0.00373	11.58	0.7016	64.33	0.0149	5.77	0.7848
15	56.59	0.00316	12.57	0.8016	70.01	0.0128	6.23	0.7185

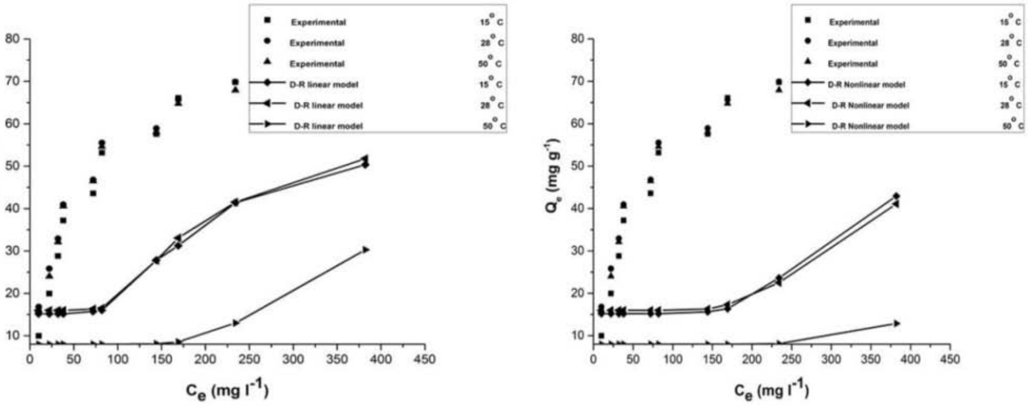

Fig. 11: Linear and Nonlinear plot of Dubinin-Raduskevich adsorption isotherm model for TC-HCl adsorption onto GAC

Surface characterization

Scanning electron microscopy (SEM) images were used to analyze the surface of the adsorbent before and after adsorption. (Fig.12a-b). An irregular porous surface of GAC before adsorption was found to be somewhat smoother after adsorption. The surface was not completely covered by TC-HCl molecules and the pores are visible after adsorption. This shows the surface has been partially occupied or there is very partial diffusion of TC-HCl in to the GAC as can been seen from the figures.

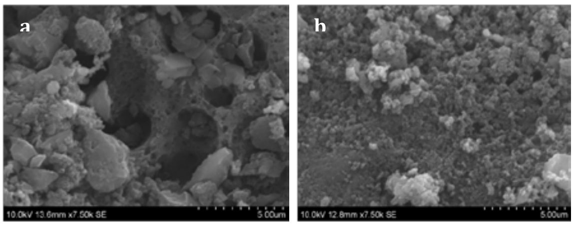

Fig. 12: (a, b) Surface elucidation of GAC after activation before and after adsorption using SEM

CONCLUSION

The main interest of the work was to know the reliance between adsorbent GAC and adsorbate TC-HCl. The effect of pH, temperature and initial concentration showed that there was a significant effect on the increasing pH, temperature and initial concentration that resulted in increase in adsorption capacity. From the thermodynamic point of view the negative values obtained for Gibbs free energy confirmed the spontaneity of the adsorption process.

The negative value of change in enthalpy and entropy proved that the adsorption process is exothermic and the enthalpy value of -22.540 kJ mol^{-1}signifies that the adsorption of TC-HCl is controlled by chemical reaction.

From the kinetic studies pseudo second order and pseudo first model gave a good fit for the adsorption process. From the isotherm studies Freundlich and Temkin's model was found to give a good fit corresponding to surface interaction which is more prevalent adsorption process of tetracycline hydrochloride as observed for various adsorbents by other researchers.

List of notations and terminology

a	Temkin isotherm constant related to equilibrium binding (L g^{-1})
b	Temkin isotherm constant (kJ mol^{-1})
B	Temkin isotherm constant related to heat of adsorption
C_i,C_f,C_e	Initial, final and equilibrium concentration (mg L^{-1})
K_{ad}	apparent equilibrium constant
K_1	1st order rate constant (min^{-1})
K_{11}	pseudo 1st order rate constant (min-1)
K_{12}	pseudo 2nd order rate constant (gmg^{-1} min^{-1})
K_F	Freundlich isotherm constant related to adsorption capacity (mg g-1)
K_L	Langmuir isotherm constant relating to affinity of binding (l mg-1)
m	mass of adsorbent (g)
n	Freundlich isotherm constant related to adsorption intensity (l/mg)
q	adsorption capacity (mg/g)
Q_{DR}	Saturation adsorption capacity (mg g^{-1})
Q_e,q_e	equilibrium adsorption capacity (mg g^{-1})
q_{exp},q_{cal}	adsorption capacity,(experimental, calculated)
Q_L	monolayer coverage capacity at equilibrium (mg g^{-1})
q_t	adsorption capacity at time t (mg g^{-1})
n	Number of degrees of freedom
p	parameter
R	universal gas constant (8.314 J mol^{-1} K^{-1})
R^2	linear regression coefficient
R_{id}	Intraparticle diffusion rate constant (mg $g^{-1}min^{-0.5}$)
R_L	Separation factor
T	temperature (Kelvin,K) (° C)
t	time (minutes)
β	Dubinin-Radushkevich isotherm constant related to the free energy of adsorption per mole of the adsorbate
ε	Polanyi potential
D-R	Dubinin-Radushkevich isotherm
TC-HCl	tetracycline hydrochloride

CONFLICT OF INTERESTS

Declared None

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