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Adsorption of antiviral drug, acyclovir from aqueous solution on powdered activated charcoal: kinetics, equilibrium, and thermodynamic studies

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ABSTRACT

The adsorption capacity of commercial powdered activated charcoal (PAC) was investigated for the removal of acyclovir from aqueous solutions. The effects of the initial acyclovir concentration (100–400 mg/L), pH (3–11), contact time, temperature (25–45°C), and PAC dose (1–4 g/L) on the removal of acyclovir have been studied. The maximum removal was found to be 98% for 100 mg/L of acyclovir solution with 4 g/L of PAC dose at 45°C. The results indicate that basic pH from 7 to 11 of acyclovir solution favored the adsorption on PAC. Moreover, the results showed that the adsorption kinetics can be represented by a pseudo-first-order model. The adsorption experimental data fitted in the order of decreasing accuracy as Freundlich, Redlich–Peterson, Temkin, Langmuir, and Dubinin–Radushkevich models. The Freundlich model was found the best to describe the equilibrium isotherm data of acyclovir adsorption on PAC. The maximum adsorption capacity of acyclovir determined from the Freundlich model was found to be 20.2 mg/g. The heat of adsorption was positive indicating endothermic nature and its low values (<70 kJ/mol) confirmed physisorption.

Keywords: Acyclovir; Powdered activated charcoal; Kinetics; Isotherm; Thermodynamics

1. Introduction

Acyclovir (9-{2-hydroxyethoxymethyl} guanine), is a synthetic nucleoside analogue, most commonly prescribed in the therapy of herpes simplex virus infections. The chemical structure (Fig. 1) consists of mainly two functional groups: alcohol and amine [1].

Acyclovir (ACV), like other antiviral drugs enter the environment through the disposal of domestic and hospital waste, pharmaceutical industries, and agricultural runoff (through soil). Its presence has also been reported in wastewater treatment plant (WWTP) discharges and surface waters [2–5]. It is largely excreted from the human body in an unchanged form via urine and feces [6]. Its concentration in wastewater effluents may also increase due to the formation of acyclovir from its prodrugs; during biological metabolism like the prodrug valacyclovir get converted into acyclovir in the human body [7] and major proportion of the drug excreted in active acyclovir form.

The environmental release of antiviral drugs has raised an alarm due to their potential harmful effects on ecosystem. Pharmaceuticals in their active form in

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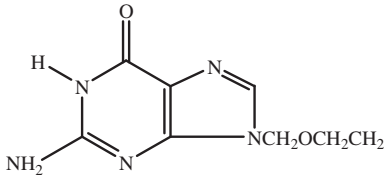

Fig. 1. Structure of acyclovir.

environment alters the genetic make-up of pathogens, hence increases the threat of the development of microbial and viral resistance. Among therapeutics, antiviral drugs are considered to be the most predicted hazardous class towards algae, daphnids, and fishes [8]. Acyclovir comes under the category of antiviral drugs, which are recognized as emerging pollutants in wastewater [9]. Acyclovir toxicity can affect central nervous system and lead to the renal dysfunction in human beings [10]. If the drug and herpes virus are concurrently present in wastewater then, the virus may become resistant to acyclovir.

Biological treatment, ozonation, and combination of membrane bioreactor and ozonation have been reported earlier for the removal of acyclovir from wastewater [2–5,11]. Although acyclovir is susceptible to biodegradation by the activated sludge microorganisms [4,5], but metabolites or transformation product has been reported to be persistent in aerobic biological treatment process [3,4]. The accumulation of small fractions of persistent organic compounds into the biological system may disturb the whole biological treatment process. Moreover, this transformation product can accumulate in sediment and soil, especially at places of wastewater discharge. The present work investigates adsorption behavior of acyclovir on PAC. Adsorption studies of acyclovir on commercial PAC have not been reported earlier for the removal of acyclovir from aqueous solution.

Removal of pharmaceuticals from effluents is a major problem for pharmaceutical industries. Physicochemical processes like ozonation, membrane filtration, chlorination, and advanced oxidation process like hydrogen peroxide (H_2O_2)-ultra-violet (UV), electrochemical destruction etc. [12–14] are costly and cannot be used by many industries and treatment plants to treat the pharmaceutical wastewater. The adsorption techniques are extensively used to remove the contaminants from wastewater and a preferred technique for the compounds that are not easily biodegradable [15]. Removal of pharmaceuticals from wastewater using adsorption has been reported in literature [16–18]. Acyclovir is a relatively recent medicine used for the treatment of Herpes infections. Adsorption being a benign and effective process for the contaminant removal has been used in the present work. The advantages of the adsorption process over other separation processes are simplicity in operation, easy recovery of adsorbate, no sludge formation, and it can be an inexpensive process as if low cost adsorbents are used [19].

In WWTP influent, the concentration of acyclovir was reported in range from 190 to 1,800 ng/L [2] and in pharmaceutical wastewaters, the concentration was reported in the range of 154–2,580 mg/L [4,5]. In the present work, the concentration of acyclovir in the range of 100–400 mg/L was taken as initial concentration due to the limitation of availability of simple and inexpensive quantitative detection technique. The proposed technique of adsorption of antiviral drug acyclovir is specifically applicable only at the source point like industrial effluent as it is feasible to remove the high concentration present at the point of discharge while, there is a possibility of the formation of transformation products after entering into environment or municipal sewage system. At the entrance of sewage treatment plant, the concentration of acyclovir is considerably reduced to ng/L due to dilution from other water bodies such as rivers, ponds etc. Removal of antiviral drugs at the industrial effluent level can be significantly achieved by this method. It will rule out any possibility of ecotoxicological effects on biological processes used at downstream process and aquatic organisms in the receiving water body. The present work reports the use of commercial powdered activated charcoal (PAC) for the adsorptive removal of acyclovir from aqueous solution. The effects of the different parameters, such as adsorbent dose (m), initial acyclovir concentration (C_0), contact time (t), temperature (T), and initial pH (pH_0) of the solution under stirred condition on the adsorption process have been investigated. The kinetics of adsorption were studied using pseudo-first-order, pseudo-second-order, intraparticle diffusion model, and elovich kinetic models. Equilibrium adsorption data have been fitted using regression analysis to isotherm model to determine the best model. The constants of kinetic models and equilibrium models have also been estimated. Moreover, thermodynamic analysis of the adsorption process has been performed and the thermodynamic parameters viz. free energy, heat of adsorption, and entropy have been determined.

2. Materials and methods

2.1. Adsorbate and other reagents

Tablets of Acivir DT 400 mg, manufactured by Cipla (India) were purchased from local pharmacy in

India. Each film-coated tablet contains 400 mg acyclovir, 40 mg starch, 20 mg talc, 30 mg magnesium stearate, and 20 mg sodium alginate [20]. Distilled water was used for the preparation of synthetic aqueous solutions of acyclovir in the initial concentration (C_0) range of 100–400 mg/L. Folin-Ciocalteu (F-C) reagent and sodium carbonate (GR Grade) were purchased from Merck (India). F-C reagent (2 N) was used directly and sodium carbonate solution (20%) was prepared in distilled water and filtered.

2.2. PAC and its characterization

The commercial grade PAC was purchased from E. Merck (India) Limited. The characteristics of the purchased commercial activated carbon vary depending upon the precursor/biomass used and activation. It was characterized, and the values obtained have been reported. The pore size distribution, specific surface area, and pore volume of PAC were carried out by N_2 adsorption using Micromeritics ASAP 2000 (Folio Instruments Inc.) by Brunauer-Emmett-Teller method. Solid addition method was used to determine pH_{zpc} [21]. Acidic and basic sites were determined by the acid-base Boehm titration method [22]. Proximate analysis of PAC was carried out using ASTM standards (3,173–3,175). The common organic elements, such as C, H, N, S, and O were analyzed in CHNSO analyzer (PerkinElmer Elementar). PAC (0.4–0.6 mg) was used in a tin boat assortment for percentage composition of C, H, N, and S analysis and the percentage oxygen was determined by means of difference.

The textural, pHzpc, proximate, ultimate, and other surface characteristics of PAC are summarized in Table 1. The pHzpc for PAC was 6.8 (Fig. 2) almost neutral in nature. The total overall acidity was calculated to be 0.31 and basicity was 0.20 mmol/g.

Fourier transform infrared (FTIR) spectroscopy of commercial PAC was carried out for determining the functional groups (Fig. 3). The pellets were prepared by mixing PAC (10 mg) with KBr (200 mg). Each spectrum was the average of 64, co-addition of scans with a total scan time 15 s in the spectral range of 1,000–4,000 cm^{-1} scanned at the rate of 8 cm^{-1}.

The band appearing at 3,441 cm^{-1} in the FTIR spectrum is assigned to hydrogen bonding; and a band appearing at 2,921 cm^{-1} corresponds to aliphatic C–H group. Peaks at 2,850 and 2,349 cm^{-1} indicate O–H stretching for carboxylic acids. Peaks at 1,579 and 1,385 cm^{-1} correspond to C=O and NO_2 (nitro) stretching, respectively. A small band appearing at 1,130 cm^{-1} is due to C–O (alcohols, ethers) bonding.

Table 1
Physicochemical characteristics of powdered activated charcoal

Parameter	Value
Textural analysis	
BET surface area (m^2/g)	1,097
Langmuir surface area (m^2/g)	1,460
External surface area (m^2/g)	400
Micropore area (m^2/g)	697
Micropore volume (cm^3/g)	0.3
Total Pore volume at P/P_o (0.9832) (cm^3/g)	0.6
Average pore diameter (nm)	1.7
pH_{zpc}	6.8
Surface functional groups (mmol/g)	
Acidic groups	0.31
Carboxylic	0.22
Lactonic	0.06
Phenolic	0.03
Basic groups	0.20
Proximate analysis	
Moisture (%)	9.43
Ash (%)	3.21
Volatile matter (%)	2.90
Fixed carbon (%)	84.50
Ultimate analysis	
C (%)	82.00
H (%)	1.82
N (%)	0.18
S (%)	0.03

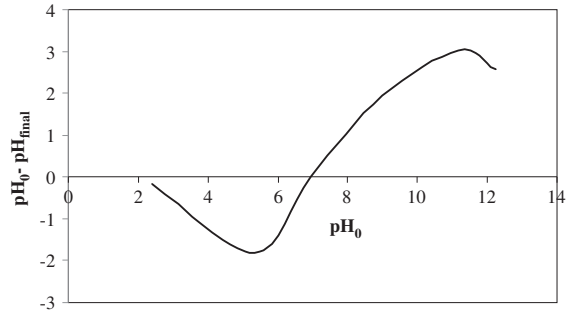

Fig. 2. Determination of pH_{zpc} of powdered activated charcoal.

X-ray diffraction (XRD) of PAC was also carried out using Bruker diffraction unit (Model D-8 Advanced Series 2) using copper radiations. The orientations were maintained at high angle, i.e. at 5 to 90°. XRD of commercial PAC is shown in Fig. 4. Minor components identified in PAC are quartz, alumina, and calcium orthosilicate, whereas, major

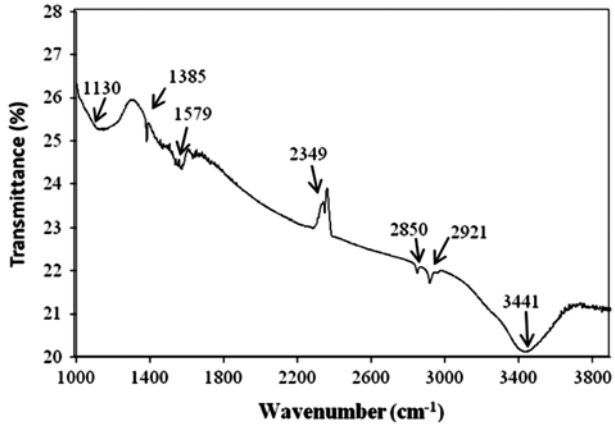

Fig. 3. Fourier transform infrared spectrum of powdered activated charcoal.

components identified are silicon oxide, wollastonite, and calcium silicate. XRD and FTIR peaks show amorphous form of silica in PAC.

A scanning electron micrograph (SEM Model JSM 840A, JEOL) having tungsten filament as electron source was used at 20 kV. SEM was used to obtain the images of virgin as well as acyclovir adsorbed PAC. The samples were mounted on a piece of double sided carbon tape, and then coated with gold film. Images were obtained at 3,500× magnification. The surface morphology of virgin as well as adsorbed PAC is shown in Fig. 5(a) and (b). The figures clearly show that the commercial PAC is highly porous, having large pore size and consists of multilayer crevices (heterogeneous surfaces). In Fig. 5(b), acyclovir-loaded PAC is easily differentiated from virgin PAC, the empty crevices or spaces have been occupied by acyclovir.

2.3. Experiments

Stock solution was prepared by adding 400 mg of drug in a volumetric flask and making the volume up

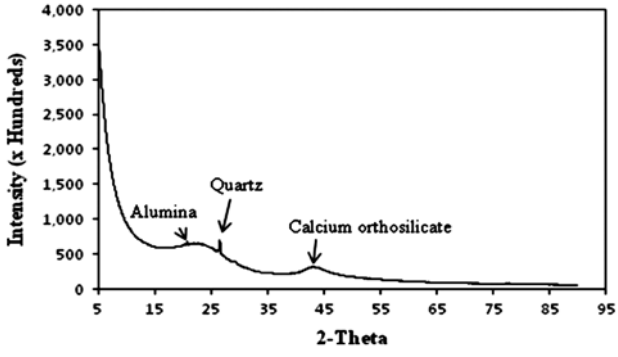

Fig. 4. X-ray diffraction pattern of powdered activated charcoal.

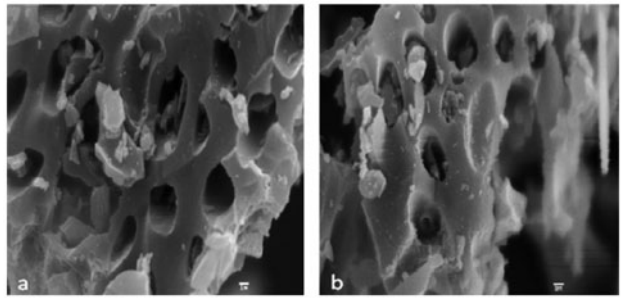

Fig. 5. Scanning electron microscopy images of (a) virgin powdered activated charcoal, (b) acyclovir adsorbed powdered activated charcoal taken at 3,500× magnification, 1 μm scale, 20 kV.

to 1 L with distilled water. The tablet was thoroughly mixed in distilled water at 600 rpm using a temperature controlled magnetic stirrer maintained at 25˚C for 60 min. Dilutions were done to obtain 100, 200, and 300 mg/L of acyclovir solutions. Fresh stock solution as required was prepared everyday and was stored in refrigerator in amber colored reagent bottle. The C_0 was ascertained by measuring absorbance using UV-vis spectrophotometer (UV1800 Shimadzu) using the method proposed by Basavaiah and Prameela [20] before the start of each experimental run. The concentration of unknown acyclovir solution was computed from the regression equation obtained from the calibration curve.

For each adsorption experiment, 200 mL of acyclovir aqueous solution of known C_0 and a known amount of PAC were taken in a 250 mL rubber-cork stoppered conical flask. This mixture was agitated in a temperature-controlled orbital shaker (Thermotech, Model TH 7004), at a constant shaking speed of 200 rpm. The percentage removal of acyclovir and the equilibrium adsorption uptake, q_e (mg/g), were calculated as:

$$\text{percentage removal of acyclovir} = \frac{(C_0 - C_e) \times 100}{C_0} \quad (1)$$

$$\text{amount of acyclovir adsorbed, } q_e \frac{(\text{mg of adsorbate})}{(\text{g of adsorbent})} = \frac{(C_0 - C_e) \times V}{m} \quad (2)$$

where C_0 is the initial acyclovir concentration (mg/L), C_e is the equilibrium acyclovir concentration (mg/L), V is the volume of the solution (mL), and m is the

mass of the adsorbent (g). Control experiments were also carried out to check for any loss of acyclovir from aqueous phase due to its volatilization at the headspace and its interaction with the stopper. The reproducibility for the adsorption of acyclovir by PAC was also studied at the optimum conditions.

The effect of adsorbent dose was studied using different doses of PAC (1–4 g/L) at constant temperature of 25˚C, contact time of 75 min, and keeping pH at 7. The effect of contact time on the removal of drug on PAC was determined for 120 min at initial acyclovir concentration of 100–400 mg/L, constant dose 4 g/L, and temperature 25˚C. The effect of temperature was studied at three different temperatures viz., 25, 35, and 45˚C using thermostat attached with a shaker (Thermotech) to control the temperature for 100 mg/L concentration, dose 4 g/L, and natural pH for 75 min. The adsorption experiments were carried out at pH range (3–11) for acyclovir concentration (100–400 mg/L) at optimum conditions which was determined at PAC dose 4 g/L at 45˚C for 75 min. The acidic and alkaline pH of the media was adjusted by adding the required amounts of 0.1 N HCl and 0.1 N NaOH. The adsorption capacities at time, q_t for different concentration were determined at definite time intervals (15 min) by keeping all other factors constant.

For reproducibility, three consecutive experiments were conducted at optimum conditions for the removal of 100 mg/L of acyclovir solution. The experimental errors for the adsorption of acyclovir were found within the standard deviation of 5.3 ± 2.5%. There was no substantial change observed in acyclovir concentration of aqueous phase during control experiments to check loss due to headspace.

2.4. Kinetic studies

Adsorption kinetics were studied for all four concentration of acyclovir (100, 200, 300, and 400 mg/L) by adding PAC (1, 2, 3, and 4 g/L) at 200 rpm at 45˚C for 75 min by collecting data at 15 min intervals. The validity of models was determined by comparing the values of standard deviation (% SD) using the following equation:

$$\%\text{S.D.} = 100\sqrt{\frac{\sum\left[(q_{\text{exp}} - q_{\text{cal}})/q_{\text{exp}}\right]^2}{n-1}} \tag{3}$$

where q_{exp} and q_{cal} are the amount of acyclovir (mg) adsorbed onto per gram of PAC determined through experimental and calculated data, n refers to the number of data points [23].

2.4.1. Pseudo-first-order model

The pseudo-first-order equation, Eq. (4) is given as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{4}$$

where q_t (mg/g) is the amount of adsorbate adsorbed at time t, q_e (mg/g) the adsorption capacity at equilibrium and k_1 (min^{-1}) is the pseudo-first-order rate constant for acyclovir adsorption [24]. Integration of Eq. (4) within appropriate limits and rearrangement yields:

$$\log\left(\frac{q_e}{q_e - q_t}\right) = \frac{k_1}{2.303}t \tag{5}$$

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{6}$$

The k_1, and q_e values were calculated by plotting the graph between log $(q_e - q_t)$ vs. t.

2.4.2. Pseudo-second-order model

The pseudo-second-order model can be represented as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{7}$$

Integrating Eq. (7) and noting that $q_t = 0$ at $t = 0$ to $q_t = q_t$ at $t = t$, the following Eq. (8) is obtained:

$$\left(\frac{t}{q_t}\right) = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}(t) \tag{8}$$

The initial adsorption rate, h (mg/g/min) is:

$$h = k_2 q_e^2 \tag{9}$$

where h, q_e, and second-order constant, k_2 (g/mg/min) can be determined experimentally from the slope and intercept, respectively, by plotting the graph between t/q_t and t.

2.4.3. Elovich kinetic model

Elovich equation considers being the most interesting model to describe the chemisorption [25]. The equation for Elovich kinetic model can be given as:

$$\frac{dq_t}{dt} = a\exp(-bq_t) \tag{10}$$

where a and b are constants. The constant, a is the initial sorption rate (mg/g/min) and b is the extent of surface coverage and activation energy for chemisorption (g/mg). Assuming $ab>>t$ and applying boundary conditions:

$$q_t = \frac{1}{b}\ln(ab) + \frac{1}{b}\ln(t) \tag{11}$$

Both a and b values were calculated by plotting the graph between q_t vs. ln (t).

2.4.4. The intraparticle diffusion model

In order to examine the mechanism of adsorption, intraparticle diffusion model has been used. The expression for intraparticle diffusion model is as follows:

$$q_t = k_d t^{0.5} + C \tag{12}$$

where k_d (mg/g/min$^{0.5}$) is the intraparticle diffusion rate constant and C (mg/g) is the intercept, which can be defined as the thickness of boundary layer. Plotting the graph between q_t and $t^{0.5}$ gives k_d and C values.

2.5. Equilibrium studies

Adsorption isotherm studies were carried out for the adsorption of acyclovir onto PAC. Equilibrium parameters obtained were analyzed by five different isotherm models, viz. Langmuir, Freundlich, Temkin, Dubinin–Radushkevich, and Redlich–Peterson model. The fitting of data in the above models were analyzed by comparing the correlation coefficients and percentage standard deviations.

2.5.1. Freundlich isotherm

The Freundlich isotherm is an empirical model and is applicable to adsorption on heterogeneous surfaces with an interaction between the adsorbed molecules [22]. It suggests that sorption energy exponentially decreases on completion of the sorptional centers of an adsorbent [24]. The Freundlich isotherm is expressed as follows:

$$q_e = K_f C_e^{1/n_f} \tag{13}$$

where K_f ((mg/g)/(mg/L)$^{1/n}$) is the Freundlich constant related to the bonding energy and can be defined as the adsorption or distribution coefficient. The $1/n_f$ is known as heterogeneity factor. It is a measure of the deviation from linearity of adsorption. The n_f value indicates the degree of nonlinearity between solution concentration and adsorption as follows: if $n_f>1$, the adsorption is a favorable physical process, if the value of $n_f=1$, the adsorption is linear; $n_f<1$, the adsorption process is chemical in nature [24]. Eq. (13) can be linearized and is expressed as:

$$\log(q_e) = \log K_f + \frac{1}{n_f}\log(C_e) \tag{14}$$

The plot of log (q_e) vs. log (C_e) gives the values of K_f and n_f.

2.5.2. Langmuir Isotherm

Langmuir equation is typically valid for adsorption of adsorbate on homogeneous surfaces of adsorbent [21]. Adsorbents that show Langmuir isotherm behavior may contain fixed individual sites, each of which equally adsorbs only one molecule of adsorbate, resulting in a monolayer formation [22]. The nonlinear form of Langmuir isotherm equation is represented as:

$$q_e = \frac{Q_L K_L C_e}{1 + K_L C_e} \tag{15}$$

The linear form of the above Eq. (15) is represented as:

$$\frac{C_e}{q_e} = \frac{1}{Q_L K_L} + \frac{C_e}{Q_L} \tag{16}$$

where C_e and q_e are as defined above in Eq. (1) and (2), respectively; K_L (L/mg) is the adsorption equilibrium constant for Langmuir isotherm that is related to the apparent energy of sorption; Q_L (mg/g) is the maximum adsorption capacity reflecting a complete monolayer. By plotting the graph between C_e/q_e and C_e gives K_L and Q_L values. Langmuir isotherm is also evaluated by a separation factor, R_L:

$$R_L = \frac{1}{1 + K_a C_0} \tag{17}$$

where C_0 in this case is the highest initial solute concentration. The value of R_L indicates the favorability of the adsorption process; if $R_L>0$, adsorption is unfavorable, if the value of $R_L=1$, adsorption is linear, if $0<R_L<1$, the adsorption process is favorable, and if $R_L=0$, adsorption is irreversible [22].

2.5.3. Temkin isotherm

This isotherm assumes that (1) the adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy, and (2) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate interactions [26]. The Temkin isotherm is represented by the following equation:

$$q_e = \frac{RT}{b_T}\ln(A_T C_e) \tag{18}$$

The linear form of Eq. (18) is as follows:

$$q_e = B_T \ln A_T + B_T \ln C_e \tag{19}$$

where $B_T = (RT)/b_T$, T (K) is the absolute temperature and R (8.314 J/mol/K) is the universal gas constant. The constant b_T is related to the heat of adsorption; A_T (min^{-1}) is the equilibrium binding constant corresponding to the maximum binding energy. The B_T (mg/g) and A_T values can be determined from plot of q_e vs. ln C_e.

2.5.4. Dubinin–Radushkevich (D–R) isotherm

The D–R isotherm model does not assume a constant sorption potential or homogeneous surface. It helps in determining the porosity apparent free energy and the characteristic of adsorption [24]. The D–R isotherm is represented by the following Eq. (20) and the linear form is shown in Eq. (21):

$$q_e = Q_m \exp(-K\varepsilon^2) \tag{20}$$

where K is a constant related to the adsorption energy, Q_m, the theoretical saturation capacity, and ε is the Polanyi potential that can be calculated using the Eq. (22):

$$\ln q_e = \ln Q_m - K\varepsilon^2 \tag{21}$$

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

The plot of ln q_e vs. ε^2 gives slope K (kJ/mol) and intercept yields the adsorption capacity, Q_m (mg/g). The mean free energy of adsorption E (kJ/mol), defined as the free energy change when one mole of ion is transferred from infinity in solution to the surface of the sorbent. The E can be calculated from the K value using the following Eq. (23):

$$E = \frac{1}{\sqrt{2K}} \tag{23}$$

2.5.5. Redlich–Peterson (R–P) model

The Redlich–Peterson (R–P) model can be used to represent the adsorption equilibria over a broad concentration range and can be useful in homogeneous or heterogeneous systems due to its versatility [27]. The three-parameter Redlich–Peterson equation which has a linear dependence on concentration in the numerator and an exponential function in the denominator [16], has been proposed to improve the fit by the Langmuir or Freundlich equation and is given by Eq. (24):

$$q_e = \frac{A_{RP} C_e}{1 + B_{RP} C_e^g} \tag{24}$$

where A_{RP} (L/g) and B_{RP} (L/mg) are R–P model constants and g is the exponent that lies between 0 and 1. If the value of $g = 1$, then it becomes Langmuir isotherm model.

2.6. Thermodynamic studies

Based on the fundamentals of thermodynamics, in an isolated system, energy cannot be gained or lost and entropy change is the only driving force. The thermodynamic parameters, such as Gibbs free energy, the value of enthalpy (heat of adsorption), and the degree of randomness, entropy for the adsorption of acyclovir onto PAC were calculated. To examine the effect of temperature in the adsorption process, both energy and entropy factors were considered in order to determine the spontaneity of the process [26]. The equilibrium constant, K_0 of the adsorption is defined as:

$$K_0 = \frac{q_e}{C_e} \tag{25}$$

Thermodynamic data such as adsorption free energy, ΔG (kJ/mol) can be obtained from Eq. (26):

$$\Delta G = -RT\ln K_0 \tag{26}$$

The thermodynamic parameters for the adsorption of acyclovir were calculated by using the following equation:

$$\ln\frac{q_e}{C_e} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{27}$$

where ΔS° (J/mol/K) is the entropy change and ΔH° (kJ/mol) is the enthalpy (heat of adsorption).

3. Results and discussion

3.1. Effect of PAC dose

The percent removal of acyclovir for all studied doses (1–4 g/L) of PAC varied from 75 to 90%. It was found that the percent removal of acyclovir was proportional to PAC dose. The percent removal increased from 78% to 90% when PAC dose increased from 1 to 4 g/L for $C_0 = 100$ mg/L (Fig. 6). This may be due to the lower dose of PAC, available sites became saturated with acyclovir molecules. It is also evident that almost 75% removal was obtained at initial acyclovir concentration of 400 with 2 g/L of PAC dose and further 10% removal was observed when PAC dose was doubled to 4 g/L. A similar behavior of adsorbent dose has been reported in case of the adsorption of acrylonitrile on activated carbon [21].

On the other hand, quantity of drug adsorbed (q_e) *vs*. adsorbent dose was studied at equilibrium (Fig. 7). As seen from the figure, the amount of drug adsorbed at equilibrium, q_e decreases with increase in PAC dose, while the adsorption capacity decreases with decrease in initial acyclovir concentration for the same PAC loading. The maximum adsorption capacity of 290 mg/g was observed when experiment was conducted with 1 g/L of PAC for adsorption of 400 mg/L of acyclovir. Increase in the drug adsorption with increase in PAC dose can be credited to increased sorbent surface area and the availability of more adsorption sites.

3.2. Effects of initial concentration of acyclovir and contact time

Fig. 8 shows the graph of the amount adsorbed of acyclovir *vs*. contact time. It may be observed from the figure that the removal of acyclovir was faster in initial stages up to 60 min, and then the process of adsorption became slower and almost constant. The rapid adsorption in initial stages can be attributed to the availability of more vacant sites on PAC. The adsorption became slower after 60 min as majority of the sites got occupied. This may be due to the repulsive forces acting between the drug molecules adsorbed and the bulk aqueous phase [21]. After 75 min, the concentration of acyclovir in the bulk phase became constant due to saturation state in PAC. Therefore, the equilibrium time observed for acyclovir adsorption onto PAC was 75 min. The removal of drug was high in low concentration ranges. It was also because of the fact, that at lower concentration, the ratio of the initial number of drug molecules to the available surface area was low subsequently the fractional adsorption becomes independent of initial concentration. However, at higher initial concentration of acyclovir, the available sites of adsorption become fewer and hence, the removal percentage of the drug depends upon the initial concentration. A subsequent

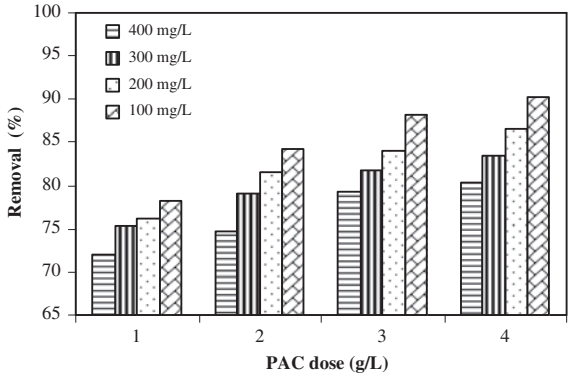

Fig. 6. Effect of PAC dose on % acyclovir removal (pH: 7, agitation speed: 200 rpm, temp.: 25°C, contact time: 75 min).

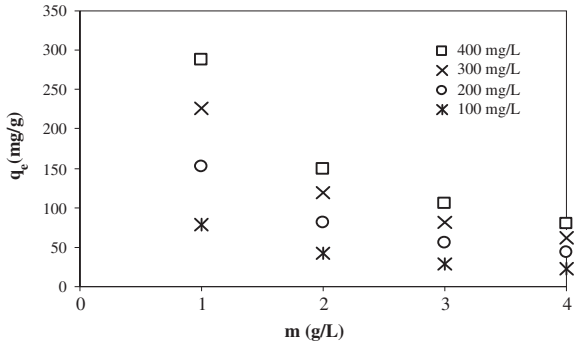

Fig. 7. Effect of PAC dose on acyclovir amount adsorbed (pH: 7, agitation speed: 200 rpm, temp.: 25°C, contact time: 75 min).

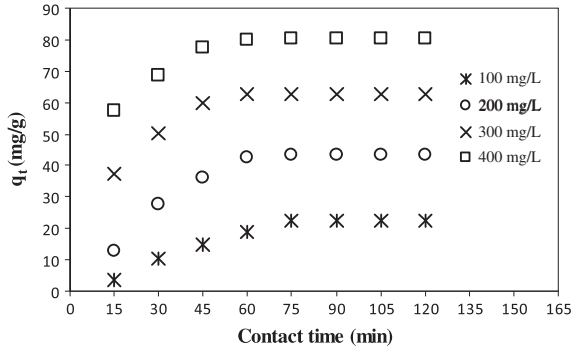

Fig. 8. Amount adsorbed, q_t (mg/g) of acyclovir vs. contact time (PAC dose: 4 g/L, pH: 7, 200 rpm, temp.: 25°C).

increase in the adsorption capacity was observed with an increase in the initial acyclovir concentration for the same PAC dose (4 g/L). At equilibrium, 80 mg/g of acyclovir was adsorbed in case of 400 mg/L of acyclovir; while only 23 mg/g was adsorbed in 100 mg/L of acyclovir solution. All the batch experiments were, therefore, conducted with a contact time of 75 min at 200 rpm.

3.3. Effect of temperature

The influence of temperature for the adsorption of acyclovir onto PAC was studied. From Fig. 9, the percent removal of acyclovir was found to increase with increase in temperature. It increased from 90% at 25°C to 98% at 45°C at an initial acyclovir concentration of 100 mg/L. Same pattern has been observed for all other three concentrations of acyclovir indicating that higher temperature favors acyclovir removal from aqueous solutions. This pattern may be attributed to increased mobility of drug molecules with temperature, which resulted in greater number of collisions between adsorbate molecules and adsorbent surface. These results were in agreement with the general adsorption process suggesting that increase in the temperature resulted in increased collisions of drug and adsorbent molecules in the solution. In turn, it increases the rate of diffusion of adsorbate molecules [23]. Therefore, the selected optimum temperature was 45°C.

3.4. Effect of pH

The wastewaters from pharmaceutical industries have a wide range of pH values [28]. Thus, pH of the system plays an important role in the treatment of pharmaceutical wastewater. With the addition of PAC adsorbent, there was no significant change observed in the pH of acyclovir solution. It may be noted in the present study that pH_{zpc} of PAC was also found to be 6.8 that is almost neutral.

Fig. 10 shows the effect of pH on the removal of acyclovir from aqueous solution. When initial pH of the drug solution was raised from 3 to 7, the percentage removal was also found to be increased from 60 to 95% for 100 mg/L of acyclovir solution. With increase in pH from 7 to 9 for the same concentration, the percentage removal slightly increased from 95 to 98%. There was a drastic increase in the percentage removal as the pH increased from 5 to 7 for all four concentrations of acyclovir. For example, in case of 400 mg/L, 85% was removed for 400 mg/L at pH 7, whereas, only 52% was removed at pH 5. There was a further decrease in the percentage removal of acyclovir at acidic pH 3. The adsorption of drug increased at pH 7, 9, and 11 due to the presence of amine moieties in acyclovir drug molecules. This contributed to its cationic nature. A similar phenomenon has been reported in case of methylene blue adsorption on beech sawdust [29]. At alkaline pH, the number of negatively charged OH^- increased, which favors the adsorption of cations due to electrostatic attraction, while excess of positively charged H^+ ions competed with the cations of drug for adsorption sites. Alkaline pH is favorable for acyclovir removal. The removal percentage values at pH 7, i.e. neutral pH were found to be comparable to those obtained at pH 11. Therefore, the results of kinetics, equilibrium, and thermodynamics will be studied at pH 7.

3.5. Adsorption kinetic studies

The kinetic parameters are helpful to determine the solute uptake rate which governs the sorption

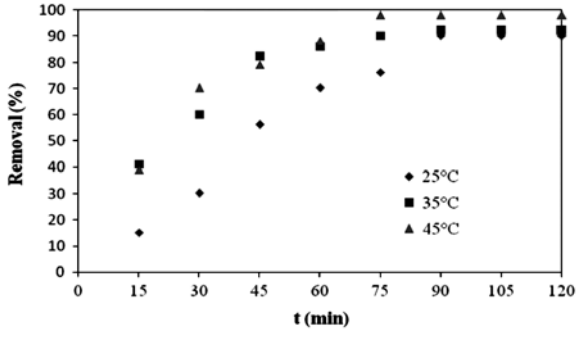

Fig. 9. Effect of temperature on % removal of acyclovir (C_0: 100 mg/L, PAC: 4 g/L, natural pH, 200 rpm, time: 75 min).

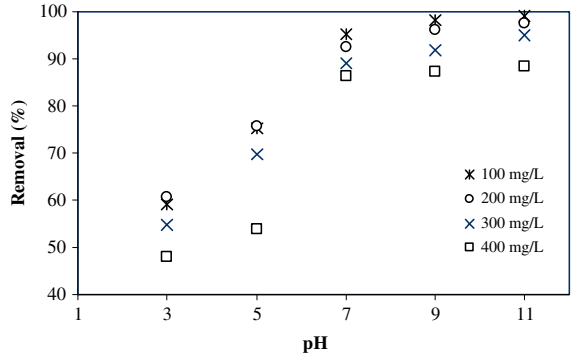

Fig. 10. Effect of pH on adsorption of acyclovir onto powdered activated charcoal (C_0: 100–400 mg/L, PAC: 4 g/L, natural pH, 200 rpm, 45°C).

process [30]. Therefore, four different kinetic models were used for the adsorption studies of acyclovir on PAC. The best fit model was selected based on the regression coefficient and standard deviation. The kinetic parameters were calculated at optimum temperature of 45°C for all four concentrations of acyclovir with all four doses of PAC at pH 7 for 75 min.

The values of kinetic parameters are shown in Tables 2 and 3. The $q_{e,exp}$ has also been compared with $q_{e,cal}$ values from both the models. More the value of R^2 and less the value of SD (%), better is the fit of the model to the system. Yet, the correlation coefficients, R^2 from all the four models were found to be high and close to unity. Hence, conclusion of best fit of data in the model has been taken on the basis of least value of standard deviation. The percent standard deviation for pseudo-first-order model was less than the other kinetic models studied. Therefore, the sorption kinetics can be represented by pseudo-first-order kinetic model followed by intraparticle diffusion model for the adsorption of acyclovir onto PAC. Moreover, the value of $q_{e,cal}$, i.e. 91.8 mg/g from pseudo-first-order model was found to be closer to the $q_{e,exp}$ value of 90.2 mg/g for 100 mg/L acyclovir solution. Similar kinetic results have been reported for the adsorption of aromatic micro-pollutants, e.g. 17β-estradiol [31] and organochlorine compounds present in an industrial effluent [32] onto activated charcoal.

In intraparticle diffusion model, the values of q_t correlated linearly with the values of $t^{1/2}$ and the rate constant, K_d directly evaluated from the slope of regression line (Fig. 11). K_d was in the range of 2.9 to 21.3 mg/g/min$^{0.5}$ and it increases with an increase in the initial acyclovir concentration. The thickness of boundary layer, C (0.3 to 41.3 mg/g) increases with increase in the adsorbate concentration (100–400 mg/L) indicating the possibility of the internal mass-transfer resistances as rate limiting step compared to external mass-transfer resistance. The deviation of the line from origin shows that intraparticle transport is not the only rate controlling step. Further, it may be attributed to boundary layer control [33].

3.6. Adsorption isotherm studies

Isotherm studies provide information on equilibrium adsorption data. It helps in evaluating the adsorption process. Parameters obtained from different models give information on the surface properties and mechanism of sorption [24]. In this study, the equilibrium data obtained for the adsorption of acyclovir onto PAC were analyzed by four linearized isotherm models, namely Langmuir, Freundlich, Temkin, Dubinin–Radushkevich models, and one nonlinearized isotherm model, Redlich–Peterson model. The applicability of isotherm models was

Table 2
Pseudo-first-order and pseudo-second-order kinetic model parameters for the adsorption of acyclovir onto powdered activated charcoal (Acyclovir conc.: 100–400 mg/L, PAC dose: 1–4 g/L, pH: 7, 200 rpm, temp.: 45°C)

PAC dose (g/L)	ACV conc. (mg/L)	Pseudo-first-order model					Pseudo-second-order model				
		$q_{e,exp}$ (mg/g)	k_1 (min^{-1})	$q_{e,cal}$ (mg/g)	R^2	SD (%)	$k_2 \times 10^4$ (g/mg/min)	$q_{e,cal}$ (mg/g)	h (mg/g/min)	R^2	SD (%)
1	100	90.2	0.04	91.8	0.991	7.4	2.0	133.3	3.6	0.990	23.9
1	200	175.2	0.04	169.6	0.975	8.9	1.2	250.0	7.7	0.986	21.4
1	300	257.2	0.03	177.0	0.991	5.2	2.2	303.0	19.9	0.996	8.9
1	400	329.2	0.05	249.2	0.958	6.2	2.5	370.4	34.7	0.997	6.3
2	100	46.6	0.03	41.3	0.976	5.7	4.1	67.6	1.9	0.978	22.5
2	200	88.6	0.03	80.8	0.976	4.4	2.6	123.5	3.9	0.986	19.7
2	300	131.1	0.03	82.6	0.985	6.5	4.2	153.9	10.0	0.994	8.7
2	400	169.1	0.03	83.4	0.986	5.3	4.7	188.7	16.9	0.993	5.8
3	100	32.4	0.03	30.9	0.968	2.4	4.1	51.8	1.1	0.953	29.9
3	200	60.1	0.04	59.5	0.982	0.5	3.3	87.7	2.5	0.986	22.9
3	300	89.1	0.04	70.1	0.973	4.7	5.9	106.4	6.8	0.995	9.7
3	400	113.7	0.04	74.7	0.868	6.2	6.5	129.9	11.6	0.987	7.1
4	100	24.6	0.03	24.7	0.987	1.2	7.1	36.9	0.9	0.981	24.8
4	200	46.3	0.04	49.6	0.999	3.5	4.3	67.6	1.9	0.995	22.9
4	300	66.8	0.05	66.1	0.963	0.5	8.8	79.4	5.6	0.999	9.4
4	400	86.3	0.05	75.9	0.917	6.0	9.7	98.0	9.4	0.994	6.8

Table 3
Elovich and Intraparticle diffusion kinetic model parameters for the adsorption of Acyclovir onto powdered activated charcoal (Acyclovir conc.: 100–400 mg/L, PAC dose: 1–4 g/L, pH: 7, 200 rpm, temp.: 45°C)

PAC	ACV	Elovich kinetic model				The intraparticle diffusion model			
Dose (g/L)	conc. (mg/L)	a (mg/g/min)	b (g/mg)	R^2	SD (%)	k_d (mg/g/min$^{0.5}$)	C (mg/g)	R^2	SD (%)
1	100	7.1	0.03	0.993	16.9	10.6	0.3	0.972	8.8
1	200	14.9	0.02	0.981	15.1	19.8	7.4	0.953	7.2
1	300	54.3	0.02	0.992	18.3	20.4	83.1	0.987	7.7
1	400	157.2	0.02	0.984	16.8	21.3	150.5	0.985	9.9
2	100	3.7	0.06	0.979	10.5	5.4	0.4	0.959	9.8
2	200	7.7	0.03	0.981	21.5	9.8	4.7	0.956	6.8
2	300	27.2	0.03	0.989	23.9	10.4	41.7	0.984	9.6
2	400	81.9	0.03	0.974	31.5	10.6	75.8	0.989	7.8
3	100	2.3	0.08	0.975	24.8	4.0	2.0	0.950	8.9
3	200	4.9	0.05	0.986	19.7	7.0	1.0	0.951	9.3
3	300	18.5	0.05	0.993	15.4	7.1	28.2	0.997	9.7
3	400	67.3	0.05	0.889	12.9	6.9	52.7	0.943	12.9
4	100	1.9	0.11	0.986	10.9	2.9	0.3	0.958	10.8
4	200	3.8	0.06	0.996	31.9	5.4	0.7	0.969	10.4
4	300	14.9	0.06	0.996	23.5	5.3	22.8	0.979	8.4
4	400	49.9	0.06	0.949	15.7	5.4	41.3	0.963	8.8

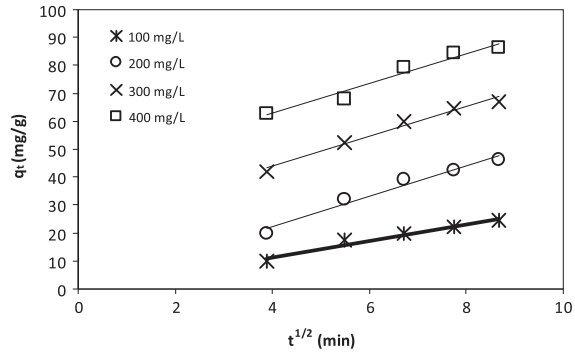

Fig. 11. Intraparticle diffusion plot for acyclovir adsorption onto powdered activated charcoal (C_0: 100–400 mg/L, PAC dose: 4 g/L, pH: 7, agitation speed: 200 rpm, temp.: 45°C).

compared by analyzing the correlation coefficients and the values of standard deviation.

From Table 4, Freundlich isotherm constants, K_f values were found to decrease with increase in PAC dose from 1 to 4 g/L. The decrease in the value may be attributed to an increase in total adsorbent surface area and pore volume available to acyclovir molecules. The trend of K_f values observed in Table 4 are in agreement with $q_{e,exp}$ values reported for different adsorbent doses depicted in Fig. 7. Freundlich constant, K_f indicates the adsorption capacity of the adsorbent and was found to be 20.2 mg/g at 45°C at equilibrium when 1 g/L PAC was used for acyclovir adsorption. In the present study, n_f values were also found to be greater than unity for all studied doses of PAC indicating that adsorption is favorable physical process [34]. The aromatic compounds are physisorbed on carbon materials essentially by dispersion interactions between the p-electrons of the aromatic ring and those of the graphene layers. Functionalization of either the adsorbent or the adsorbate profoundly affects these dispersion interactions [35].

The monolayer capacities of acyclovir onto PAC at 45°C were found to be 588.2, 263.2, 138.9, and 98.0 mg/g at 1, 2, 3, and 4 g/L of PAC doses, respectively. These results indicate that the monolayer capacity decreased with increase in PAC dose which supports the conclusion drawn from K_f value of Freundlich isotherm. Also, in the present study, R_L value varied from 0 to 1, therefore, the adsorption of acyclovir onto PAC is a favorable process. K_a is known as the adsorption equilibrium constant for Langmuir isotherm related to the apparent energy of sorption. It is a measure of the strength of the bonds formed during adsorption. The value of K_a was found to increase with increase in temperature. These indicate that the bonds formed at 45°C between PAC and acyclovir was stronger than those formed at 25 and 35°C.

From Table 5, A_T, the equilibrium binding constant was found to decrease with increase in PAC dose at 25 and 45°C. A_T corresponds to the maximum binding

Table 4
Adsorption isotherm parameters for Freundlich and Langmuir models for Acyclovir- powdered activated charcoal system (Acyclovir conc.: 100–400 mg/L, PAC dose: 1–4 g/L, pH: 7, 200 rpm, temp.: 25–45°C)

Temp. (°C)	PAC dose (g/L)	Freundlich model				Langmuir model				
		n_f (–)	K_f (mg/g)/(mg/L)$^{1/n}$	R^2	SD (%)	Q_m (mg/g)	K_a (L/mg)	R_L * (–)	R^2	SD (%)
25	1	1.2	6.5	0.995	0.4	833.3	0.01	0.33	0.966	7.7
25	2	1.4	6.4	0.992	3.9	285.7	0.01	0.20	0.998	13.6
25	3	1.5	5.8	0.999	2.9	192.3	0.01	0.20	0.969	14.9
25	4	1.6	5.7	0.999	1.4	128.2	0.02	0.11	0.987	13.1
35	1	1.6	18.9	0.969	2.3	500.0	0.02	0.12	0.978	14.4
35	2	1.4	7.5	0.982	3.6	357.1	0.01	0.20	0.975	12.3
35	3	1.4	5.3	0.995	3.5	243.9	0.01	0.20	0.988	14.6
35	4	1.6	6.3	0.997	1.0	142.9	0.02	0.10	0.968	14.3
45	1	1.5	20.2	0.995	2.2	588.2	0.02	0.12	0.995	14.7
45	2	1.7	14.8	0.995	3.8	263.2	0.03	0.10	0.942	15.8
45	3	2.5	20.4	0.971	1.9	138.9	0.06	0.04	0.914	16.9
45	4	2.8	19.2	0.985	5.9	98.0	0.09	0.03	0.945	13.5

*400 mg/L acyclovir solution.

energy that decreases linearly with coverage due to adsorbate–adsorbate interactions. The value of the adsorption capacity, B_T was also found to decrease with increase in PAC dose. The mean free energy of adsorption E increased with increase in PAC dose at 25, 35, and 45°C. The value of the adsorption capacity, Q_m was also found to decrease with increase in PAC dose. The Redlich–Peterson model can be used to represent the adsorption equilibria over a broad concentration range and can be useful in homogeneous or heterogeneous systems due to its versatility [27].

Therefore, the sorption isotherm can be represented by the Freundlich model followed by the Temkin model for the adsorption of acyclovir onto PAC. From the Freundlich isotherm, it could be assumed that the stronger binding sites are occupied first; and then the binding strengths are decreased with increasing degree of site occupation [36]. In the present study, n_f values were also found to be greater than unity for all doses of PAC indicating that the adsorption was a favorable physical process. The agreement of equilibrium data of Freundlich isotherm model for the adsorption of acyclovir onto PAC indicates that sorption energy exponentially decreased on completion of the sorptional centers of PAC. Therefore, the Freundlich isotherm is valid for this acyclovir-PAC system.

The correlation coefficient, R^2 was found high for all studied linearized and nonlinear isotherm models. Considering the high R^2 values and almost equal SD (%) values of Freundlich isotherm model in comparison to other isotherm models, experimental data fit better in the Freundlich model for PAC. Moreover, the values of correlation coefficients, R^2 for these isotherms were found high than those for Langmuir, Temkin, Dubinin–Radushkevich, and Redlich–Peterson isotherm models. Considering high R^2 and low SD (%) values, the adsorption experimental data fitted in the order of: Freundlich > Redlich–Peterson > Temkin > Langmuir > Dubinin–Radushkevich model. The Freundlich and Redlich–Peterson isotherm models were found to best fitted among all the models, indicating that sorption energy exponentially decreased on completion of the sorptional centers of PAC. The comparison of the results obtained from Freundlich model for the removal of acyclovir onto PAC with the data reported in literature for antibiotics and hazardous chemical are represented in Table 6. The n_f values for the adsorption of acyclovir onto PAC were comparable with the n_f values reported for antibiotics [16,17] and hazardous chemical, acrylonitrile [21]. This indicated that the adsorption of acyclovir onto PAC was a favorable physical process and followed the general trend of adsorption of a few antibiotics. In addition to this, the K_f values for the adsorption of acyclovir onto PAC lie within the range reported for antibiotics.

3.7. Adsorption thermodynamic studies

Thermodynamic parameters for the adsorption of acyclovir onto PAC are summarized in Table 8.

Table 5
Adsorption isotherm parameters for Temkin, Dubinin–Radushkevich, and Redlich–Peterson models for Acyclovir-powdered activated charcoal system (ACV: 100–400 mg/L, PAC: 1–4 g/L, natural pH, 200 rpm, temp.: 25–45°C)

Temp. (°C)	PAC dose (g/L)	Temkin model					Dubinin–Radushkevich model					Redlich–Peterson model				
		A_T (L/g)	B_T (mg/g)	b_T (–)	R^2	SD (%)	Q_m (mg/g)	$K \times 10^{-6}$ (kmol^2/J^2)	E (kJ/mol)	R^2	SD (%)	A_{RP} (L/g)	B_{RP} (L/mg)	g (–)	R^2	SD (%)
25	1	0.7	128.9	19.2	0.981	4.4	249.6	100	70.7	0.902	6.5	3.4	0.02	0.9	0.974	1.4
25	2	0.6	58.2	42.6	0.991	11.4	127.7	50	100.0	0.902	17.5	5.9	0.45	0.5	0.987	0.8
25	3	0.6	38.4	64.6	0.967	11.3	86.0	30	129.1	0.864	15.0	5.3	0.36	0.6	0.979	0.1
25	4	0.5	27.3	90.8	0.979	10.5	65.4	20	158.1	0.872	14.7	9.8	0.03	0.9	0.966	2.7
35	1	0.6	110.6	23.2	0.992	9.3	268.6	30	129.1	0.936	18.6	3.9	0.01	1.5	0.959	1.0
35	2	0.6	67.6	37.9	0.997	9.9	143.6	30	129.1	0.925	20.3	2.9	0.01	1.1	0.975	0.7
35	3	0.6	44.7	57.3	0.979	8.4	93.2	20	158.1	0.897	18.1	11.4	0.05	0.4	0.987	1.5
35	4	0.5	29.2	87.7	0.967	6.7	67.8	10	223.6	0.855	14.4	10.8	0.02	0.9	0.965	0.7
45	1	0.5	121.0	21.9	0.985	4.9	272.9	20	158.1	0.884	16.3	29.9	0.90	0.4	0.984	0.5
45	2	0.4	54.5	48.5	0.949	8.8	133.2	8	250.0	0.834	12.9	11.6	0.51	0.5	0.951	4.1
45	3	2.2	25.3	104.7	0.895	7.9	85.6	2	500.0	0.786	9.2	11.6	0.60	0.6	0.938	4.6
45	4	4.9	16.9	156.7	0.912	10.4	83.4	2	158.1	0.920	18.2	7.4	0.28	0.4	0.995	1.5

Acyclovir adsorption on PAC was found to be endothermic in nature requiring some amount of activation as the value of ΔH° was found to be positive. Moreover, value of ΔH° varied from 16.4 to 69.5 kJ/mol indicating physisorption [30]. These results were found to be in agreement with Freundlich isotherm model, which also suggests that the adsorption process was physical in nature. The positive value of ΔS° suggested increased randomness at the solid/solution interface during the adsorption of acyclovir onto PAC. The entropy value was also found to decrease with increase in acyclovir concentration and almost consistent for all four doses of PAC. The Gibb's free energy of the process at all temperatures was found to be negative and increased with rise in temperature. The negative values of Gibb's free energy at all studied temperatures indicated spontaneity of the adsorption process and thermodynamically favorable. The results are in agreement with the R_L values reported earlier in Table 4, which showed the adsorption of acyclovir onto PAC a favorable process. Moreover, the values of Gibb's free energy in the −20 to 0 kJ/mol range correspond to spontaneous physical processes, while those with values in the −80 to −400 kJ/mol range corresponds to chemisorption [37]. For the adsorption of acyclovir onto PAC, the values of Gibb's free energy lies within the range of −6.9 to 0 kJ/mol further confirming the physisorption (Table 7).

3.8. Comparison of present adsorption study with the available literature for removal of acyclovir from wastewater

Table 8 represents the comparison of the reported removal processes for acyclovir from wastewater in the present study. Ninety eight percent removal of acyclovir was reported after 12 days from wastewater when treated with German conventional wastewater treatment technique [2]. The biotransformation product, carboxy-acyclovir (carboxy-ACV) obtained during biological treatment of acyclovir was also reported and found to be biologically persistent under aerobic conditions [3]. Mascolo et al. studied the removal of acyclovir through biological treatment [4] and also through the integrated system consisting of membrane bioreactor (MBR) and ozonation [5]. A combination of MBR with ozonation resulted in 99.99% removal of ACV in the effluent MBR stream. Investigators also reported that one compound was persistent during biodegradation of acyclovir. Although chemical and biological methods are quite effective for the removal of pollutants from

Table 6
Comparison of reported values of Freundlich parameters for the adsorption of various adsorbates by commercial activated carbon

Adsorbate (Category)	PACdose (g/L)	Temp. (°C)	Parameters/constants			PACh dose (g/L)
			K_f (mg/g)/ (mg/L)$^{1/n}$	n_f (–)	R^2	
Penicillin G (Antibiotic)	1	25	6.4	1	25	[16]
	1	35	14.5	1	35	
	1	45	4.3	1	45	
Metronidazole (Antibiotic)	1	25	403.3	1	25	[17]
Dimetridazole (Antibiotic)	1	25	408.9	1	25	
Tinidazole (Antibiotic)	1	25	268.5	1	25	
Ronidazole (Antibiotic)	1	25	479.4	1	25	
Acrylonitrile (Hazardous chemical)	20	35	2.7	20	35	[21]
	20	40	2.5	20	40	
	20	50	2.4	20	50	
Acyclovir (Antiviral drug)	4	25	5.7	4	25	Present work
	4	35	6.3	4	35	
	4	45	19.2	4	45	

Table 7
Thermodynamic parameters for adsorption of Acyclovir-PAC system (ACV: 100–400 mg/L, PAC: 1–4 g/L, natural pH, 200 rpm, temp.: 298–318 K)

PAC dose (g/L)	ACV conc. (mg/L)	R^2	ΔH° (kJ/mol)	ΔS° (J/mol/K)	$-\Delta G$ (kJ/mol) at temperatures		
					298 K	308 K	318 K
1	100	0.966	37.3	136.0	3.2	4.9	5.9
1	200	0.846	31.6	116.6	2.9	4.8	5.2
1	300	0.996	26.5	98.1	2.8	3.7	4.7
1	400	0.999	23.2	85.8	2.3	3.2	4.1
2	100	0.968	37.1	132.2	2.4	3.4	5.1
2	200	0.885	22.3	81.8	2.0	3.2	3.6
2	300	0.925	24.1	86.5	1.6	2.8	3.3
2	400	0.941	24.2	84.9	1.0	2.2	2.7
3	100	0.783	59.9	206.8	2.3	2.6	6.5
3	200	0.994	21.4	76.3	1.4	2.1	2.9
3	300	0.999	23.6	82.6	1.0	1.8	2.6
3	400	0.981	16.4	57.2	0.6	1.3	1.7
4	100	0.839	69.5	238.5	2.1	2.8	6.9
4	200	0.929	25.9	90.5	1.2	1.7	3.0
4	300	0.971	19.1	66.2	0.6	1.4	1.9
4	400	0.982	17.2	58.0	0.0	0.8	1.2

wastewater but they are energy intensive, time consuming, need expensive equipment, and often end up with generation of by-products. Furthermore, oxidation often produces degradation by-products (DBPs) which may be eco-toxic also. Unlike, other chemical treatment techniques, adsorptive removal has been proved to be a clean technology for the removal of pharmaceuticals from wastewater. Activated carbon can be regenerated easily using thermal, chemical or solvent regeneration.

Table 8
Removal of Acyclovir through different treatment processes reported in literature

S. No.	Treatment process	Concentration of Acyclovir	Main findings	Reference
1.	German conventional wastewater treatment plants (WWTPs)	190 ng/L	98% removal was reported with hydraulic retention time (HRT) of 12 h and sludge retention time (SRT) of 10–12 days, respectively	[2]
2.	Activated sludge treatment; biotransformation	1,800 ± 300 ng/L	Almost 92% removal and one transformation product (TP) (Carboxy-Acyclovir) were reported	[3]
3.	Aerobic biological treatment (activated sludge)	170–2,580 mg/L	Acyclovir powders and one metabolite have reported to be not completely biodegradable	[4]
4.	Integrated membrane bioreactor (MBR)-Ozonation system	154 mg/L	99% removal with the MBR and further 99% removal of residual Acyclovir were reported when MBR integrated with Ozonation was used	[5]
5.	Ozonation	12 mg/L dissolved organic carbon (DOC) and pH 7.7	N-(4-carbamoyl-2-imino-5-oxoimidazolidin)-formamido-N-methoxyacetic acid (COFA) as oxidation product of acyclovir	[11]
6.	Adsorption	100–400 mg/L	80–98% removal is observed for the range of 100–400 mg/L acyclovir solution in 75 min	Present study

4. Conclusions

The present study shows that the powdered activated charcoal (PAC) is effective for the removal of acyclovir from aqueous solution. Higher percentage of acyclovir removal by PAC was observed when the concentration of acyclovir in solution was kept low. Optimum PAC dose is 4 g/L at alkaline pH 11 and 45˚C under stirred conditions. The equilibrium time for acyclovir adsorption onto PAC was 75 min. Adsorption kinetics followed pseudo-first-order rate model. The thickness of boundary layer increases with increase in adsorbate concentration (100–400 mg/L). The Freundlich isotherm was found to be the best-fitted isotherm model. The adsorption of acyclovir increases with increase in temperature and positive value of ΔH° indicates endothermic nature of the adsorption process. Negative values of free energy at all studied temperatures indicate that the adsorption process is spontaneous and favorable for acyclovir removal. Positive value of entropy suggests increased randomness at the solid/solution interface. This indicates that the adsorption of acyclovir onto PAC is more at higher temperatures. In conclusion, acyclovir is significantly adsorbed by PAC from the aqueous solution.

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