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Kinetics and isotherm studies on the adsorption of an antiparkinsonism drug Entacapone from aqueous solutions using unsaturated polyester resin (UPR)

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ABSTRACT

Growing concern about environmental issues has prompted the pharmaceutical industry to investigate appropriate and environmentally friendly treatment technologies. Removal of pharmaceuticals by adsorption is one of the most promising techniques, due to its convenience. In the present communication adsorption of Entacapone from wastewater using low-cost non-carbon adsorbent unsaturated polyester resin (UPR) has been reported. Results showed that adsorption of Entacapone onto UPR have some advantages such as high adsorption capacity and short adsorption time. Different thermodynamic parameters like Gibb's free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) of the undergoing process have also evaluated through these adsorption models. The estimated values for ΔG° were $-11.953 \times 10^{3}\,\mathrm{kJ\,mol^{-1}}$ over UPR at 303 K (30 °C) indicate toward a spontaneous process. The rate equations showed that the adsorption kinetic data generally fitted the rate equations from which the rate constants and diffusion rate constants were evaluated. However, the Lagergren pseudo first-order rate equation gave the best fit, and thus the process followed first-order rate kinetics.

Keywords: Adsorption; Kinetics; Isotherms; Entacapone; UPR

1. Introduction

Water contamination with small concentrations of pollutants, such as pharmaceuticals, hormones, and pesticides, are a serious problem [1–4]. Pharmaceuticals are now attracting attention as a potentially new class of water pollutant. Such drugs as antibiotics, anti-depressants, anti-parkinsonism, birth control pills, seizure medicines, cancer treatments, pain killers, tranquilizers, and cholesterol-lowering compounds have been detected in varied water sources [5–8]. People often dispose of unused medicines by flushing them down toilets, and human excreta can contain various incompletely metabolized agents. They may be extremely dangerous for the environment because they are able to perform adverse biological effects on living organisms, sometimes in a non-predictable manner. Today, there are over 10,000 drugs available commercially, most of which are non-biodegradable because of their stability toward light and oxidation; also these drugs are resistant to aerobic digestion due to their complex aromatic molecular structure and synthetic origin. Pharmaceutical industries, hospitals, and other medical facilities are obvious sources. Various physical and chemical techniques like coagulation, adsorption, chemical oxidation, and froth flotation processes have

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been used by a number of research workers for the removal of organics as well as inorganic from wastewaters, as discussed in the review article of Bailey et al. [9].

For the past few years, our laboratory has exploited inexpensive adsorbents, such as gram husk [10], saw dust [11], de-oiled mustard [12–14], wheat husk [15], rice husk [16], and coconut husk [17,18] as efficient and suitable adsorbents for the removal and recovery of hazardous dyes [19–23]. Literature survey reveals that a large number of such waste products like bagasse fly ash [24], bottom ash [25,26], de-oiled soya [27,28], rice husk [29], etc. have been utilized as potential adsorbent. Gupta et al. [30–36] and Mittal et al. [37–44] have also utilized various adsorbents for removal of dyes from wastewater.

Entacapone is a nitrocatechol-structured compound. It is therapeutically classified as a selective, reversible, and peripheral inhibitor of catechol-O-methyl transferase. It is given as adjunctive therapy to patient with parkinson's disease. Entacapone may be given as combination preparation with carbidopa and levodopa; this will extend the effect and duration of levodopa in the brain and allows levodopa to be given less often and in lower doses [45]. The most frequent undesirable effects caused by Entacapone relate to the increased effects of L-DOPA, such as involuntary movements (dyskinesias) [46]. These occur most frequently at the beginning of Entacapone treatment. Others common side effects are gastrointestinal problems, including nausea and abdominal pains. In studies with Entacapone, some people have reported experiencing a dry mouth.

The main objectives of this paper are: (i) to study the feasibility of using unsaturated polyester resin (UPR) as an adsorbent for the removal of Entacapone: an antiparkinsonism drug, (ii) to determine the various parameters affecting sorption, such as pH, adsorbent dose, initial concentration, contact time, and temperature, (iii) to evaluate the usefulness of various kinetic models, viz. pseudo-first-order, pseudo-second-order, and intraparticle diffusion models, and (iv) to determine the applicability of linear and non-linear forms for various isotherm models (i.e. Freundlich, Langmuir, and Tempkin). The developed method is easy, versatile, and economical due to its simple operation, design, and low cost.

2. Materials and methods

The drug under consideration Entacapone (Fig. 1) sodium 4-[(2E)-2-(oxonaphthalen-1-ylidene) hydrazinyl] benzene sulfonate (molecular formula $C_{16}H_9N_4Na_3O_9S_2$, molecular weight 350.33 g mol^{-1})

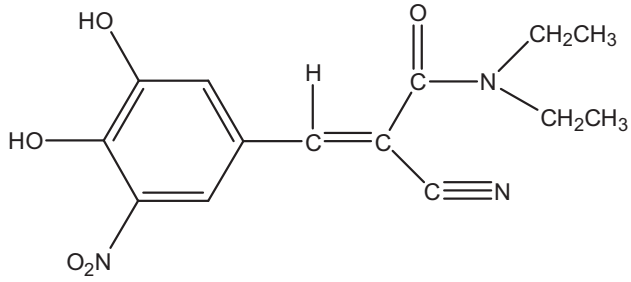

Fig. 1. Structure of Entacapone.

was obtained from Sun Pharma. Standard solution of the drug was prepared in 0.01 N sodium hydroxide. Various solutions at desired concentrations were prepared from standard solution. Sodium hydroxide was used for necessary dilutions. All reagents used in the present work were of analytical grade. Adsorbent UPR was obtained from M/s Naphtha Resins, Bangalore, India, and was used without any purification. Measurements of pH of the solutions were carried out on a digital pH meter (DB 1011 India). Adsorption measurements were recorded on a Systronics spectrophotometer 166 (India) over the wavelength range 325–990 nm.

2.1. Adsorption studies

Adsorption was determined by a batch method, which permits convenient evaluation of parameters that influence the adsorption process. In the batch method, a fixed amount of the adsorbent (9 mg) was added to 30 mL of Entacapone solution of varying concentrations (0.04–0.16 mg/mL), taken in 100-mL conical flasks. The solutions were stirred continuously at constant temperatures. The samples were withdrawn after equilibrium time (determined initially) and the drug solution was separated from the adsorbent using Whatman filter paper (No. 42). The Entacapone removal was determined spectrophotometrically at maximum absorbance λ_{max} 350 nm.

2.2. Isotherm studies

Isotherm studies were carried out using a fixed mass of UPR adsorbent (9 mg) in contact with 30 mL of drug solution in a 100 mL graduated conical flask. The desired concentration of drug solution was prepared by dilution of the stock solution with 0.01 N NaOH solution. The conical flasks were sealed and agitated in a water bath shaking apparatus at different temperatures (30, 40, and 50 °C) until equilibrium. At time $t = 0$ and equilibrium, the concentration retained

in the adsorbent phase (q_e, mg g^{-1}) was calculated by the following equation:

$$q_e = (C_0 - C_e)\, W/V \quad (1)$$

where C_0 and C_e are the initial and equilibrium adsorbate concentrations (mg L^{-1}), respectively. V is the volume of solution (L) and W is the mass of adsorbent (g).

2.3. Quality assurance/quality control

Accuracy is necessary in an experiment; so all of the batch isotherm tests were replicated thrice to establish the accuracy, reliability, and reproducibility of the collected data. In different experiments, blanks were run and corrections were made wherever necessary. All glasswares used in the study were prepared by soaking in 5% HNO_3 solution for a period of 3 days before being doubly rinsed with distilled, deionized water, and oven dried.

3. Results and discussion

3.1. Adsorbent characterization

In the present study, SEM photograph of UPR reveals surface texture and porosity. SEM was performed using a Zeiss EVO 50 instrument. Powder X-ray diffraction (XRD) measurements were performed on Diffractometer system XPERT-PRO X-ray powder diffractometer using a graphite monochromatic with Cu Ka radiation ($k = 1.5406$ Å). XRD pattern at 2θ that ranges between 10° and 70° was used for phase characterization. XRD pattern exhibits sharp diffraction peak at 2θ and 10°, which indicates that particles are crystalline in nature.

3.2. The effect of adsorbent dose on adsorption process

To optimize the adsorbent dose for the removal of Entacapone from its aqueous solutions, adsorption was carried out with different adsorbent dosages at different temperatures. The dose of adsorbent was varied from 0.1 to 0.8 g/L for UPR at a fixed pH, temperature, and adsorbate concentration. The study shows an increase in adsorption with the increase in dosage of the adsorbent. As the adsorbent dosage increases, the adsorbent sites available for the drug molecules also increase and consequently better adsorption takes place [47]. Thus, in all subsequent studies, the optimum amount of UPR was chosen as 0.3 g/L. At this amount, the adsorption over UPR is efficient and save unnecessary use of excess of adsorbent quantity wise. The half-life of the process was also determined at varying doses for UPR and it was specified that the half-life increases with increasing amount. As shown in (Fig. 2) for UPR, with increasing amount of sorbent, sorption percent of the drug is also increased gradually. About 95% of drug sorption was observed for 9 mg of sorbent dosage. After that the increase is very little. Such a trend is mainly due to increase in sportive surface area and availability of more exchangeable sites for drug.

3.3. Effect of temperature

In addition, change in temperature will change the equilibrium capacity of the adsorbent for a particular adsorbate. The removal of Entacapone increases from 47.2 to 57.9 mg g^{-1} by increasing the temperature of the solution from 30 to 50°C, indicating that the process is endothermic. It is apparent that the maximum adsorption for UPR occurred at 50°C and adsorption follows the order 30 < 40 < 50°C.

4. Adsorption isotherms

At equilibrium, adsorption isotherm helps to provide important information on the adsorption mechanisms, the surface properties, and affinities of the adsorbent. The Langmuir, Freundlich, and Tempkin isotherm equations were applied in this study. The linear regression is frequently used to determine the best-fitting isotherm and the applicability of isotherm equations is compared by judging the correlation coefficients.

4.1. Langmuir isotherm

Adsorption isotherm data have been described by the Langmuir adsorption isotherm [48]. Langmuir

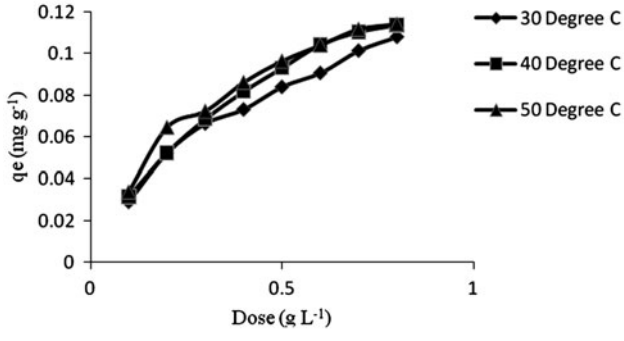

Fig. 2. Effect of amount of adsorbent for the removal of Entacapone by UPR 0.3 g/L at pH 10.5 and different temperatures.

isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies of adsorption with no transmigration of adsorbate in the plane of surface. The linear form of the isotherm was analyzed in the light of the Langmuir model.

$$1/q_e = 1/Q^0 + 1/bQ^0C_e \quad (2)$$

where q_e is the amount adsorbed (mol g^{-1}) and C_e is the equilibrium concentration of the adsorbate (mol L^{-1}). Q^0 and b are the Langmuir constants related to maximum adsorption capacity and energy adsorption, respectively. When $1/q_e$ is plotted against $1/C_e$, a straight line with slope $1/bQ^0$ is obtained, which shows that the adsorption of Entacapone over UPR follows the Langmuir isotherms. Langmuir constants are calculated and values of these constants at different temperatures are given in Table 1. It must be pointed out that Q^0 and b are empirical constants and are really secondary parameters obtained graphically using Eq. (2). So, a definite conclusion regarding the trend cannot be obtained by comparing b and Q^0 values separately. In such cases, the better alternative is to compare bQ^0 value which shows the same trend as shown in Table 1.

Table 1
Langmuir and Freundlich isotherms for Entacapone over UPR at pH 10.5 and different temperatures, and Tempkin isotherm for Entacapone over UPR at pH 10.5 and 30°C

Langmuir isotherms for Entacapone over UPR					
Temp.	b (mol g^{-1})	Q^0 (L mol^{-1})	bQ^0	R^2	% RSD*
30°C	2.531	0.220	115.04	0.810	0.75
40°C	5.494	0.023	238.86	0.953	1.13
50°C	5.952	0.023	258.78	0.910	1.39
Freundlich isotherms for Entacapone over UPR					
Temp.	K_f	ns	R^2	% RSD*	
30°C	1.275	2.906	0.858	0.98	
40°C	1.388	3.048	0.975	1.03	
50°C	1.374	3.144	0.977	1.15	
Tempkin isotherms for Entacapone over UPR					
Temp.	B (J mol^{-1})	A (L g^{-1})	B	R^2	
30°C	3.916	50.199	9127.326	0.969	

*Average of three replicate measurements.

The essential characteristics of the Langmuir isotherm can be expressed in terms of the dimensionless constant separation factor for equilibrium parameter, R_L [49], defined as follows:

$$R_L = 1/(1 + bC_0) \quad (3)$$

where C_0 is the initial concentration of the drug and b is the Langmuir constant. The values of R_L indicate the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$), or unfavorable ($R_L > 1$). Values of separation factor for the adsorbent are found to be less than unity, confirming thereby the favorable adsorption process. The same method has already been adopted [50] to confirm the favorability of a Langmuir type of adsorption.

4.2. Freundlich isotherms

The adsorption data for adsorption over UPR were also found to be fitted to the linear form of the Freundlich equation [51]. The well-known logarithmic form of Freundlich isotherm is given by the following equation:

$$\log q_e = \log K_f + 1/n \log C_e \quad (4)$$

where q_e is the amount adsorbed (mol g^{-1}) and C_e is the equilibrium concentration of the adsorbate (mol L^{-1}). K_f and n are Freundlich constants with n giving an indication of how favorable the adsorption process and K_f [mg/g (l/mg)$^{1/n}$] is the adsorption capacity of the adsorbent. K_f can be defined as the adsorption or distribution coefficient and represents the quantity of drug adsorbed onto UPR for a unit equilibrium concentration (Table 1). The slope of $1/n$ ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero [52]. The value of $1/n$ below one indicates a normal Langmuir isotherm while $1/n$ above one is indicative of cooperative adsorption. Result from this experiment shows the n values ranging between 1 and 10, indicating beneficial adsorption. Linear plot of log q_e vs. log C_e shows that the adsorption of Entacapone from an aqueous solution on UPR also follows Freundlich isotherms. Similar observations were reported for the adsorption of Direct Red 12B dye on biogas residual slurry [53].

4.3. Tempkin isotherms

Tempkin and Pyzhev [54] contain a factor that explicitly takes into account the adsorbent–adsorbate

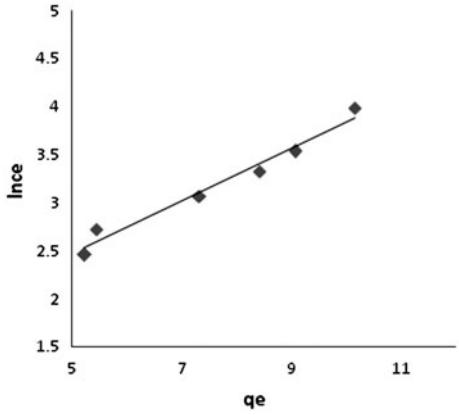

Fig. 3. Tempkin adsorption isotherms for adsorption of Entacapone by UPR at pH 10.5 and 30°C.

interactions (Fig. 3). The heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to adsorbent–adsorbate interactions. The Tempkin model is linearly represented as Eq. (5) and generally applied in the form:

$$q_e = B\,(\ln A) + B\,(\ln C_e) \tag{5}$$

where A and B are the Tempkin isotherm constant (l/g) and heat of sorption (J/mol), respectively (Table 1). R is the gas constant (J/mol K) and b is the Tempkin isotherm constant linked to the energy parameter, B, as shown in Eq. (6)

$$b = RT/B \tag{6}$$

T is the absolute temperature in Kelvin. The quantity, b, has no unit as justified by the unit relationship in Eq. (7) below:

$$b = (\mathrm{Jmol^{-1}K^{-1}K})/\mathrm{Jmol^{-1}} \tag{7}$$

4.4. Thermodynamic parameters

Thermodynamic parameters were evaluated to confirm the adsorption nature of the present study. The thermodynamic constants, Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy change (ΔS°) are calculated to evaluate the thermodynamic feasibility and the spontaneous nature of the process. The change in enthalpy (ΔH°) and entropy (ΔS°) can be calculated from the variation of Langmuir constant with temperature (T) using the following thermodynamic relations [55].

$$\Delta G^\circ = -RT \ln b \tag{8}$$

$$\Delta H^\circ = -R(T_2T_1)/(T_2 - T_1) \ln (b_2/b_1) \tag{9}$$

$$\Delta S^\circ = (\Delta H^\circ - \Delta G^\circ)/T \tag{10}$$

where b, b_1, b_2 are the equilibrium constants at different temperatures, which are gathered from the slopes of straight lines obtained in case of Langmuir adsorption isotherms at different temperatures. Negative free energy values for UPR system indicate the spontaneity of the adsorption process. It was also seen that ΔG° values decrease with increasing temperatures, which once again reveals higher adsorption at higher temperatures (Table 2). Endothermic nature [56,57] of the process was once again confirmed by obtaining positive values of ΔH° and good affinity of the UPR towards the Entacapone is shown by positive ΔS°.

5. Adsorption kinetics

The kinetic study of adsorption processes provides useful data regarding the efficiency of the adsorption and the feasibility for scale-up operations. The kinetic data of adsorption can be evaluated using different types of mathematical models of which the one most widely used is Lagergren's rate equation. The kinetics of the adsorption process was analyzed using the first-order rate equation [58].

$$\log (q_e - q_t) = \log q_e - k_{ad} \times t/2.303 \tag{11}$$

where q_e and q_t signify the amount adsorbed at equilibrium and at any time t, respectively. Lagergren's plots for Entacapone adsorption over UPR at

Table 2
Thermodynamics Parameters of Entacapone over UPR at pH 10.5 and different temperatures

	ΔG° (kJ mol^{-1})			ΔH° (kJ mol^{-1})	ΔS° (JK^{-1} mol^{-1})
Adsorbent	30°C	40°C	50°C	30°C	30°C
UPR	-11.953×10^3	-3.946×10^3	-4.132×10^3	6.468×10^3	60.79

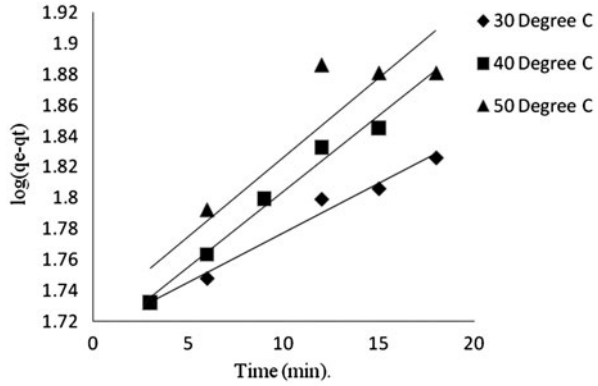

Fig. 4. Lagergren plots for adsorption of Entacapone over UPR at pH 10.5 and different temperatures.

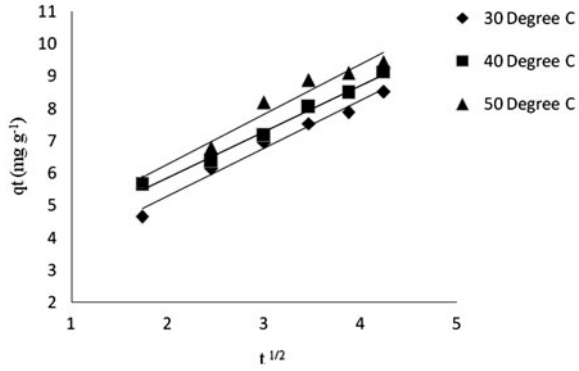

Fig. 5. Intraparticle diffusion plot for Entacapone adsorption over UPR at pH 10.5 and different temperatures.

Table 3
Rate constants k_{ad} for Entacapone over UPR at pH 10.5 and different temperatures

	UPR	
Temperature (°C)	k_{ad}	%RSD*
30	0.0138	0.983
40	0.0207	0.980
50	0.0230	0.963

*Average of three replicate measurements.

Table 4
Intraparticle diffusion coefficients and intercept values for Entacapone adsorption on UPR at pH 10.5 and different temperatures

	UPR		
Temperature (°C)	k_{dif}	C	R^2
30	1.472	2.345	0.981
40	1.414	3.050	0.990
50	1.539	3.202	0.963

pH 10.5 and different temperatures for UPR obtained for $\log(q_e - q_t)$ vs. t exhibit straight lines and confirm the adsorption process to follow first-order rate kinetics (Fig. 4). The k_{ad} values evaluated from the respective Lagergren's plot are presented in Table 3. The correlation coefficients for the pseudo-second-order kinetic model are <0.95, indicating a poor pseudo-second-order fit to the experimental data.

5.1. The intraparticle diffusion model

The intraparticle diffusion is another kinetic model which should be used to study the rate of the drug adsorption onto UPR. The possibility of intraparticle diffusion was explored by using the intraparticle diffusion model, which is expressed by the following equation:

$$q_t = K_{dif} t^{1/2} + C \quad (12)$$

where C (mg g^{-1}) is the intercept and K_{dif} is the intraparticle diffusion rate constant (in mg g^{-1} min$^{-1/2}$). The values of q_t were found to be linearly correlated with values of $t^{1/2}$ (Fig. 5) and the rate constant K_{dif} directly evaluated from the slope of the regression line. The values of intercept C provide information about the thickness of the boundary layer, the resistance to the external mass transfer increases as the intercept increases. The constant C was increased with increasing the drug concentration, which indicate the increase of the thickness of the boundary layer and decrease of the chance of the external mass transfer and hence increase of the chance of internal mass transfer. R^2 values given in Table 4 are close to unity indicating the application of this model. This may confirm that the rate-limiting step is the intraparticle diffusion process. The linearity of the plots demonstrated that intraparticle diffusion played a significant role in the uptake of the adsorbate by adsorbent.

6. Conclusion

Adsorption of Entacapone on the surface of adsorbent has been found to be an efficient and economically cheap process. In the present study, UPR was used as an adsorbent for the removal of Entacapone

drug from an aqueous solution. The UPR has very high adsorption capacity to remove the drug, with a monolayer adsorption capacity. The adsorption increases with the increase in amount of adsorbent. Freundlich, Langmuir, and Tempkin equations agreed very well with the equilibrium isotherms. A pseudo-first-order kinetic model agreed well with the dynamical behavior for the adsorption of Entacapone drug on UPR under different temperatures, consistent with physical adsorption being the rate-limiting step.

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