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Adsorption study of tetracycline onto an unsaturated polyester resin

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ABSTRACT

The present work was aimed to study the adsorption of tetracycline, an antibiotic drug. Adsorption studies were performed on adsorptive unsaturated polyester resin (UPR) at temperatures 30, 40, and 50°C. It is a low-cost potential effective absorbent and can be used to remove antibiotic tetracycline from aqueous solution. The preliminary investigations were carried out by batch adsorption. The experimental equilibrium data were tested by four widely used isotherm models namely, Langmuir, Freundlich, Tempkin, and Dubinin–Radushkevich. Thermodynamic parameters such as standard enthalpy (ΔH°), standard entropy (ΔS°), and standard free energy (ΔG°) were determined. The negative value for ΔG° is indicating towards a spontaneous process and the positive value for ΔH° indicates that the adsorption of tetracycline to UPR is an endothermic process. The adsorption process followed pseudo-first-order model. The mass transfer property of the sorption process was studied using Lagergren pseudo-first-order kinetic models. The values of percentage removal and k_{ad} for drug systems were calculated at different temperatures (303–323 K). The mechanism of the adsorption process was determined from the intraparticle diffusion model. The results indicate that UPR can be used as an effective and low-cost adsorbent to remove tetracycline from aqueous solution.

Keywords: Adsorption; Kinetics; Isotherms; Tetracycline; Unsaturated polyester resin

1. Introduction

Antibiotics have attracted increasing concern in recent years, because they have been proved to be a class of potent pollutants [1,2]. The principal sources of antibiotics and other drugs in the environment are from pharmaceutical industry, intensive farming, and human excretion residues [3]. Antibiotics from the tetracycline family have been extensively used in human and veterinary medicine to treat and prevent bacterial infections. Residues of these antibiotics discharged from agricultural run-off and municipal wastewater treatment plants are frequently detected in soil, surface water, groundwater, and even drinking water [4]. Antibiotics can also have a direct effect on the environment by disrupting ecosystem equilibrium [5]. Natural bacteria exposed to residual antibiotics could modify their genetic information developing higher antibiotic resistance and resulting in multi-resistant strains of micro-organisms [6]. Due to their antibacterial nature, antibiotic residues, or contaminated waters cannot be effectively eliminated by traditional biological methods [7,8]. On the other hand, advanced oxidation processes have proved to be a suitable alternative

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for rapid degradation of recalcitrant and non-biodegradable compounds in water [9–11]. Their use in salmon production has been reported [12], and it has been established that their excessive accumulation can produce arthropathy, nephropathy, central nervous system alterations, spermatogenesis anomalies, possible mutagenecity, and photosensitivity in human beings [7]. Significant amounts of these antibiotics have been found in animal tissues and in wastewater [13]. Specifically, the tetracycline antibiotics, a group of commonly used antibiotics, have been shown to disrupt microbial soil respiration [14], Fe(III) reduction [15], nitrification [16], and phosphatase activities [14]. The widespread use of tetracyclines have become a serious problem since they are substances that leave residues in milk or meat, which can be directly toxic or else cause allergic reactions in some hypersensitive individuals. Even more important, low-level doses of antibiotic in foodstuffs consumed for long periods can lead to problems regarding the spread of drug-resistant micro-organisms. To ensure human food safety, maximum residue limits have been set for tetracycline, chlortetracycline, and oxytetracycline in a number of tissue types, including 0.3 mg kg^{-1} in liver, 0.6 mg kg^{-1} in kidney, 0.2 mg kg^{-1} in eggs, and 0.1 mg kg^{-1} in milk and muscle tissues [17,18]. The removal of pharmaceutical antibiotics by conventional water and wastewater treatment technologies is generally incomplete. A number of techniques namely coagulation, precipitation, filtration, reverse osmosis, ion exchange, adsorption, and photocatalytic degradation have been used to remove toxic compounds from the aquatic environment. However, there is still an increasing demand for the development of efficient and cost-effective treatment technologies for the removal of such pollutants. Adsorption is a rapid phenomenon of passive sequestration and separation of adsorbate from aqueous/gaseous phase on to solid phase. This process is noted to be superior to other removal techniques because it is economical, simple and it is capable to efficiently treat drugs in more concentrated form. Choice of adsorbent is one of the key factors determining the effectiveness of any adsorption process. The important aspect of adsorption processes is easy regenerability and less operational cost. Scientists investigated the adsorption and removal of tetracycline antibiotics by several materials, including smectite clay [19], montmorillonite [20], rectorite [21], palygorskite [22], chitosan particles [23], aluminum oxide [24], coal humic acid [25], activated carbon [26], single-walled carbon nanotubes and multi-walled carbon nanotubes [27], metal or metal oxides [28], magnesium–aluminum hydrotalcite [29], hydrous oxides of aluminum and iron [30], and iron oxides and iron oxide-rich soils [31], but the use of these adsorbents is limited because of their high price, high operating costs, and problems with regeneration hamper its large scale applications. The objective of the present investigation is to overcome this problem by using a non-carbon adsorbent unsaturated polyester resin (UPR) for the removal of antibiotic tetracycline. In environmental engineering, polymers have been used for different purposes, but the use of natural polymers has attracted considerable attention from the perspectives of cost, environmental concern, and safety. UPR are produced by the polycondensation of saturated and unsaturated dicarboxylic acids with glycols. UPR form highly durable structures and coatings when they are cross-linked with a vinylic reactive monomer, most commonly styrene. The properties of the cross-linked UPRs depend on the types of acids and glycols used and their relative proportions. UPR is easily available, cheap, and economically advantageous. Jain et al. [32–34] have also utilized UPR for removal of dyes and pharmaceuticals from wastewater. In the present study, application of UPR for the removal of tetracycline from aqueous solution has been studied. Batch method has been performed to measure the amounts of equilibrium adsorption. Kinetic models, viz. pseudo-first-order and intraparticle diffusion models, and various isotherm models (i.e. Freundlich, Langmuir, Tempkin, and Dubinin–Radushkevich), have also been evaluated. From the results, it is concluded that developed method is easy, versatile, and economical due to its simple operation, design, and low cost.

2. Materials and methods

2.1. Chemicals and reagents

Tetracycline (Fig. 1) is chemically 4-(dimethyl amino)-1,4,4a,5,5a,6,11,12a-octa hydro-3,6,10,12,12a-penta hydroxy-6-methyl-1,11-dioxo-2-naphthacene-carboxamide. Tetracycline ($C_{16}H_{18}N_3SCl$) was chosen as adsorbate and purchased from Merck with water

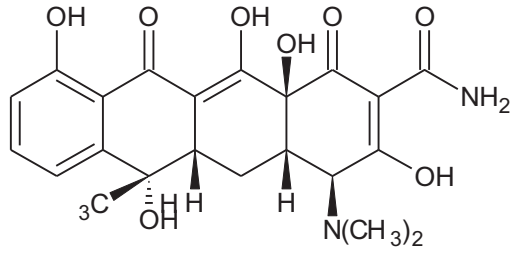

Fig. 1. Structure of tetracycline.

solubility as 50 g L^{-1} (20°C) and molecular weight as 319.85 g mol^{-1}. The drug stock solution was prepared by dissolving accurately weighted tetracycline in distilled water to the concentration of 100 mg L^{-1}. Adsorbent UPR was obtained from M/s Naphtha Resins, Bangalore, India, and were used without any purification. Distilled water was used throughout the investigation. Folin–Ciocalteu (F–C) reagent (Merck, India) and sodium carbonate (S.D. Fine Chem Ltd, India) were of analytical reagent grade and used without further purification. The commercially available F–C reagent was diluted with water in a ratio 1:1. Working concentration of drug solution was prepared by dilution of the above stock solution with 1.4 M Na_2CO_3 and F–C reagent (1:1). All reagents used in the present work were of analytical grade. A Systronics model 166 digital spectrophotometer (Systronics Ltd, India) over the wavelength range 325–990 nm with matched 1-cm quartz cells was used to measure absorbance of the resulting solutions. Sartorius CP224S analytical balance (Gottingen, Germany) and ultra sonic cleaner (Frontline FS 4, Mumbai, India) were used during the study. Measurements of pH of the solutions were carried out on a digital pH meter (DB 1011 India).

2.2. Absorption spectra

Pure TETRA solution equivalent to 0.55 mg mL^{-1} was mixed with 3 mL of 1.4 mol L^{-1} Na_2CO_3 and 2 mL of F–C reagent (1:1) in a 50-mL volumetric flask. After 20 min, the volume was made up to the mark with water and the contents were mixed thoroughly. In the same way, a blank solution was prepared in the absence of drug. The blank was measured against water. Maximum absorbance was obtained at 700 nm and was fixed as analytical wavelength.

2.3. Adsorption and kinetic studies

All adsorption measurements were carried out through batch technique at 30, 40, and 50°C temperatures and desired pH. In each measurement, 30 mL of the working solution of drug of desired concentration and appropriate amounts of adsorbent were taken in a 100 mL graduated airtight conical flask and mechanically agitated intermittently, till the equilibrium was established. However, in case of kinetic measurements, the flask was shaken only for the desired time period. The adsorbents were now removed from the solution after carefully filtering by Whatmann filter paper (No. 41) and the concentration of the drug was determined on spectrophotometer at λ_{max} 700 nm. The amount of drug adsorbed onto the UPR, q_e (mg/g), was calculated by a mass balance relationship Eq. (1).

$$q_e = \frac{(C_o - C_e) \times W}{V} \quad (1)$$

where C_o and C_e are the initial and equilibrium liquid-phase concentrations of drug, respectively (mg/L), V is the volume of the solution (L), and W is the weight of the UPR used (g).

2.4. Quality assurance/quality control

To establish the accuracy, reliability, and reproducibility of the collected data, all batch isotherm tests were replicated twice, and experimental blanks were run in parallel. All jars, conical flasks, and containers used in the study were prepared by being soaked in 5% HNO_3 for a period of 3 d before being rinsed thrice with distilled deionized water and oven-dried. The precision of the analytical procedures expressed as the relative standard deviation (RSD) ranged from 5 to 10%. In different experiments, blanks were run, and corrections were applied if necessary. All observations were recorded in triplicate, and average values and their standard deviations are reported.

2.5. Adsorption mechanism

Selection of the most promising types of adsorbent, particularly in terms of its efficiency and low cost is the first major challenge for adsorption field. The next challenge is to clearly identify the adsorption mechanism(s), in particular, the interactions occurring at the adsorbent/adsorbate interface. The nature of the reaction depends upon several parameters related to the adsorbent, to the solution pH, and the chemistry of the targeted compound. The adsorption process of the adsorbate molecules from the bulk liquid phase into the adsorbent surface is presumed to involve the following stages:

(1) Mass transfer of the adsorbate molecules across the external boundary layer towards the solid particle.
(2) Adsorbate molecules transport from the particle surface into the active sites by diffusion within the pore-filled liquid and migrate along the solid surface of the pore.
(3) Solute molecules adsorption on the active sites on the interior surfaces of the pores.
(4) Once the molecule adsorbed, it may migrate on the pore surface through surface diffusion [35].

3. Results and discussion

3.1. Adsorbent characterization

The UPR was analyzed by scanning electron microscope (SEM), powder X-ray diffraction (XRD) and Fourier transform infrared (FTIR). SEM photograph of UPR is shown in Fig. 2. SEM is widely used to study the morphological features and surface characteristics of the adsorbent materials. In the present study, SEM photograph of UPR reveals surface texture and porosity. SEM was performed using a Zeiss EVO 50 instrument. Powder XRD measurements were performed on Diffractometer system XPERT-PRO X-ray powder diffract meter using a graphite monochromatic with Cu Ka radiation ($k = 1.5406$ Å). XRD pattern at 2θ ranges between 10° and 70° was used to phase characterization. XRD pattern (Fig. 3) of UPR exhibits sharp diffraction peak at $2\theta = 10°$, which indicates that particles are crystalline in nature. The FTIR spectra are shown in Fig. 4. In Infrared spectra of UPR shows strong peak absorbance at 2,920 and 2,848 cm^{-1} due to methylene stretching. Strong peak absorbance at 1,650 cm^{-1} also indicated presence of carbonyl group. >C=C< stretching was observed at lower frequency 1,468 cm^{-1}. Characteristics peak absorbance observed at 1,046 cm^{-1} was due to presence of C–O stretching of ester group. =C–H (alkene) bending was also observed at 916 cm^{-1}.

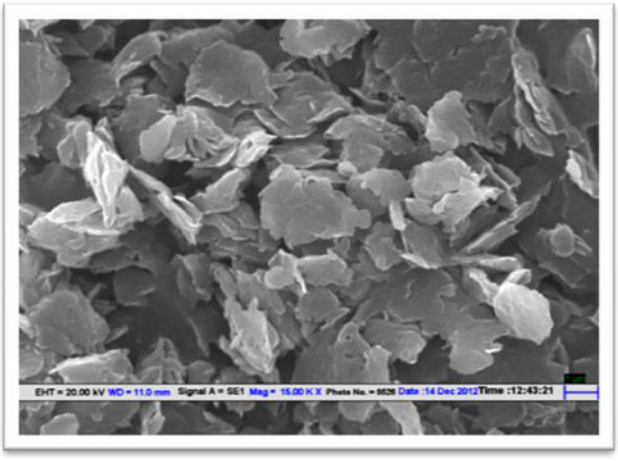

Fig. 2. SEM photograph of UPR.

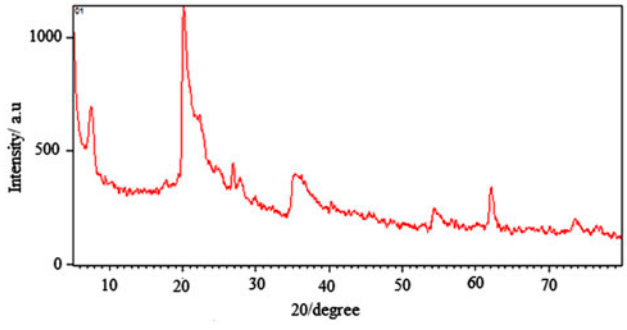

Fig. 3. XRD pattern of UPR.

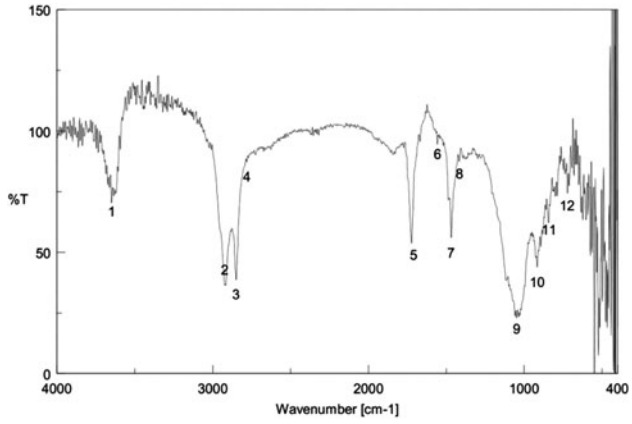

Fig. 4. FTIR spectra of UPR.

3.2. Effect of amount of adsorbent

As the adsorbent dosage increases, the adsorbent sites available for the drug molecule also increases and consequently better adsorption takes place. In the present study, the adsorbent doses were varied from 0.66 to 2.66 g L^{-1} for UPR at fixed pH 10.1, adsorbate concentration 0.55 mg mL^{-1}, and different temperatures. It is apparent that initially the rate of increase in

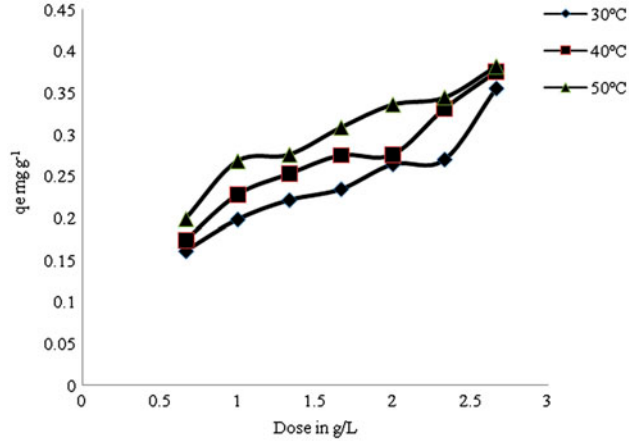

Fig. 5. Effect of amount of adsorbent for the removal of tetracycline by UPR 2 g L^{-1} at pH 10.1 and different temperatures.

the percentage of drug removal has been found to be rapid from 0.66 to 0.266 g L^{-1} (Fig. 5). This phenomenon can be explained based upon the fact that at lower adsorbent dose the adsorbate is more easily accessible and because of this removal per unit weight of adsorbent is higher. The initial rise in adsorption with adsorbent dose is probably due to a stronger driving force and large surface area. Hence, for all subsequent studies, adsorbent dose 2 g L^{-1} was found to be optimum.

4. Adsorption isotherms

Adsorption isotherms are very important for the optimization of the adsorption system. The equilibrium relationship between adsorbent and adsorbate are best explained. There are several isotherm models viz. Freundlich, Langmuir, Tempkin, and Dubinin–Raduskevich (D–R) isotherms are available for analyzing experimental data and for describing the equilibrium of adsorption.

Freundlich isotherm is based on the assumption that the adsorption occurs on heterogeneous surfaces with interaction between adsorbed molecules and suggests that adsorption energy has a non-uniform distribution over the adsorbent surface. This isotherm is an empirical equation which can be employed to describe heterogeneous systems and is expressed in linear form by the following equation:

$$\log q_e = \log k_f + 1/n \log C_e \quad (2)$$

where q_e is the amount adsorbed (mol g^{-1}), C_e is the equilibrium concentration of the adsorbate (mol L^{-1}), and K_f and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively [36]. When log q_e is plotted against log C_e at three different temperatures, (30, 40, and 50) ℃, straight lines with slope $1/n$ are obtained.

The Langmuir isotherm is derived on the assumption of monolayer coverage of adsorbate over a homogenous adsorbent surface [37,38]. The linear form of the Langmuir isotherm is given by the following:

$$1/q_e = 1/Q^0 + 1/bQ^0C_e \quad (3)$$

where q_e is the amount adsorbed (mol g^{-1}), C_e is the equilibrium concentration of the adsorbate (mol L^{-1}), and Q^o and b is Langmuir constants related to maximum adsorption capacity and energy of adsorption, respectively. When $1/q_e$ is plotted against $1/C_e$, a straight line with slope $1/bQ^o$ is obtained, which shows that the adsorption of tetracycline follows Langmuir isotherm. Langmuir constants are calculated and values of these constants at different temperatures are given in Table 1. As a result UPR has higher

Table 1
Freundlich, Langmuir, D–R, and Tempkin isotherm for tetracycline over UPR at different temperature

Temp. (℃)	K_f	N	R^2	%RSD[#]	
Freundlich constants for tetracycline over UPR					
30	1.336596	0.840	0.985	0.810	
40	1.559553	1.261	0.975	0.909	
50	1.489361	1.121	0.984	0.920	
Langmuir constants for tetracycline over UPR					
Temp. (℃)	b (mol g^{-1})	Q^o(L mol^{-1})	bQ^o	R^2	%RSD[#]
30	0.719	0.011	65.36	0.941	0.936
40	1.135	0.014	81.07	0.936	0.838
50	1.280	0.015	85.34	0.938	0.808
D–R Constants for tetracycline over UPR					
Temp. (℃)	B_D	E	q_D	R^2	
30	12.66	0.198	30.33	0.974	
40	15.20	0.181	35.48	0.908	
50	15.42	0.180	37.05	0.881	
Tempkin isotherms for tetracycline over UPR					
Temp. (℃)	B (J mol^{-1})	A (L g^{-1})	B	R^2	
30	1.240741	3.4556	7775.13 0.999	0.969	

[#]Average of three replicate measurements.

adsorption capacity for tetracycline as compared to Kaolinite [39].

Tempkin isotherm model [40] contains a factor that explicitly takes into account of adsorbing species–adsorbate interactions. This model assumes the following: (i) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent–adsorbate interactions, and that (ii) the adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy. The derivation of Tempkin isotherm assumes that the fall in the heat of sorption is linear rather than logarithmic, as implied in the Freundlich equation (Fig. 6a). The Tempkin isotherm has commonly been applied in the following form:

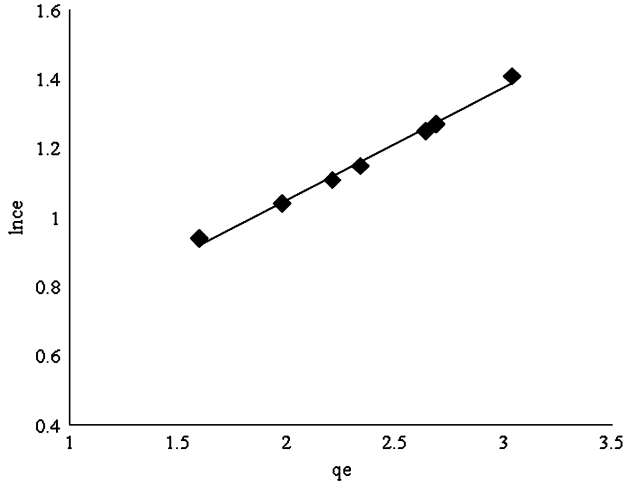

Fig. 6a. Tempkin adsorption isotherms for adsorption of tetracycline over a UPR at 30°C.

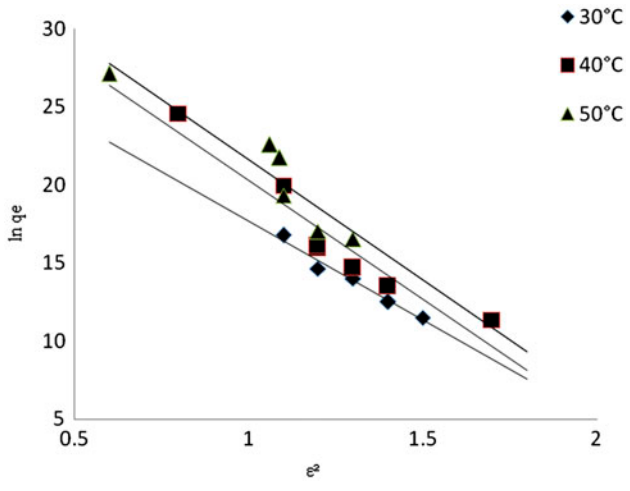

Fig. 6b. Dubinin–Raduskevich (D–R) isotherms of tetracycline for UPR at pH 10.1.

$$Q_e = \frac{RT}{bT} + ln\,(AC_e) \tag{4}$$

where RT/bT = B (J mol^{-1}), which is the Tempkin constant related to heat of sorption, whereas A (L g^{-1}) is the equilibrium binding constant corresponding to the maximum binding energy. R (8.314 J mol^{-1} K) is the universal gas constant and T (K) is the absolute solution temperature.

The D–R isotherm is more general because it does not assume a homogenous surface or constant adsorption potential [41]. It was applied to estimate the porosity, apparent free energy, and the characteristics of adsorption. The linear form can be represented as:

$$\ln q_e = \ln q_D - B\varepsilon^2 \tag{5}$$

where B is a constant related to the mean free energy of adsorption (mol^2(kJ^2)$^{-1}$), q_D is the theoretical saturation capacity (mg g^{-1}), ε is the polyani potential, and calculated as follows:

$$\varepsilon = \mathrm{RT}\,ln(1 + 1/C_e) \tag{6}$$

The slope of the plot of lnq_e vs. ε gives B and the intercept yields the adsorption capacity, q_D. Fig. 6b shows D–R plot and the results are given in Table 1. The mean free energy of adsorption (E) (kJmol^{-1}) is calculated from the Eq. (7);

$$E = 1/(2B)^{0.5} \tag{7}$$

5. Thermodynamic parameters

Thermodynamic parameters obtained for both adsorption systems were also calculated using the following equations:

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

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

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \tag{10}$$

where b, b_1, and b_2 are the equilibrium constants at different temperatures, which are obtained from the

Table 2
Thermodynamic parameters of tetracycline over UPR

Adsorbent	ΔG^o (kJ mol^{-1})			ΔH^o (kJ mol^{-1})	ΔS^o (JK^{-1} mol^{-1})
	30℃	40℃	50℃	30℃	30℃
UPR	-10.52×10^3	-11.43×10^3	-11.93×10^3	35.30×10^2	46.39

slopes of straight lines from Langmuir adsorption isotherms at different temperatures, R (8.314 J mol^{-1} K) is the universal gas constant and T (K) is the absolute solution temperature. Negative value of ΔG^o indicates feasible and spontaneous nature of the ongoing adsorption process. It is also observed that in each case, ΔG^o value decreases with the increasing temperature, indicating thereby greater adsorption at higher temperature. Endothermic nature of the process was once again confirmed by the positive values of ΔH^o (Table 2).

6. Adsorption kinetic studies

The pseudo-first-order kinetic model has been widely used to predict sorption kinetics [42]. The model given by Langergren and Svenska [43] is defined as:

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

where q_e and q_t (mg g^{-1}) are the amounts of adsorbate adsorbed at equilibrium and at any time, t (h), respectively, and k_1 (1/h) is the adsorption rate constant. The plot of ln ($q_e - q_t$) vs. t as shown in Fig. 7a gave the slope of k_{ad} and intercept of log q_e. The values of

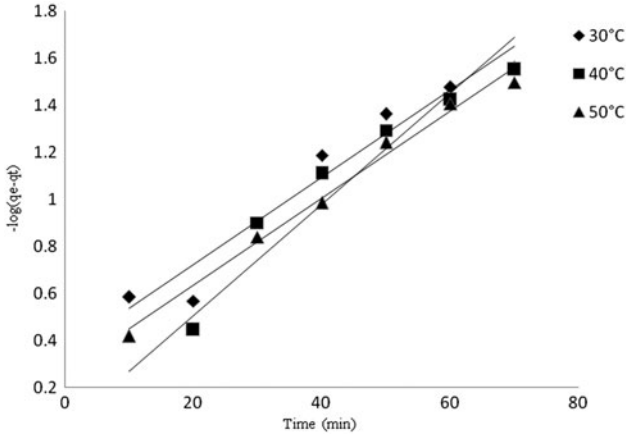

Fig. 7a. Lagergren plots for adsorption of tetracycline of UPR at pH 10.1 and different temperatures.

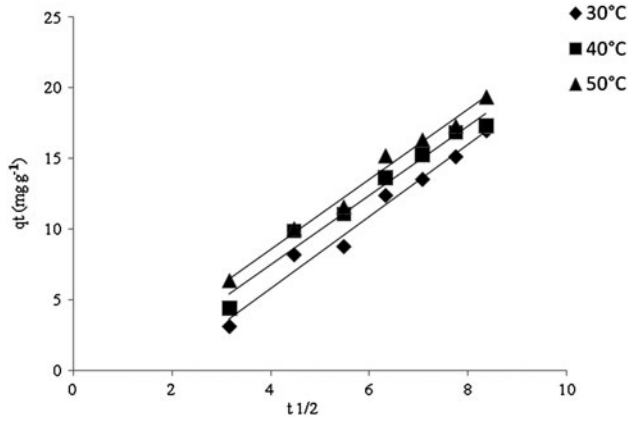

Fig. 7b. Intraparticle diffusion plot for tetracycline adsorption on UPR at different temperatures.

k_{ad} and correlation coefficient, R^2 obtained from the plots for adsorption of tetracycline on the UPR at 30℃ are given in Table 3. The slope of each straight line gave value of the rate constant, k_{ad} at that temperature. An increase in values of k_{ad} further confirms the

Table 3
Rate constants and intraparticle diffusion coefficients and intercept value for tetracycline over UPR at pH 10.1 and different temperatures

Rate constants for tetracycline over UPR

Temp. (℃)	k_{ad}	%RSD[#]
30	0.041454	0.983
40	0.052969	0.980
50	0.043757	0.963

Intraparticle diffusion coefficients and intercept value for tetracycline over UPR

Temp. (℃)	Unsaturated polyester Resin (UPR)		
	k_{dif}	C	R^2
30	2.544	4.378	0.979
40	2.442	2.284	0.971
50	2.473	1.343	0.987

[#]Average of three replicate measurements.

increase in uptake of drug at increasing temperature. The k_{ad} values evaluated, for each system, from the respective Lagergren 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.

6.1. Intraparticle diffusion model

Weber and Chakkravorti [44] suggested a kinetic model to identify the diffusion mechanisms and rate controlling steps that affect the adsorption process. It is empirically a functional relationship, common to most adsorption processes, where uptake varies almost proportionally with $t^{1/2}$ rather than with the contact time. According to this theory, the intraparticle diffusion equation is expressed as follows:

$$q_t = K_{id}\,(t^{1/2}) + C \tag{12}$$

where q_t adsorbate uptake at time t, (mg g^{-1}), K_{id} the rate constant of intraparticle transport, (mg g^{-1}-$t^{1/2}$) and C is the intercept (mg g^{-1}). The plot of q_t vs. $t^{1/2}$ gives a straight line from which k_{id} can be calculated from the slope of the plot. Values of C give an idea about the thickness of boundary layer, i.e. the larger the intercept, greater the contribution of the surface sorption in the rate controlling step. The data for the adsorption of tetracycline onto UPR applied to intraparticle diffusion model is shown in Fig. 7b and the results are presented in Table 3.

7. Conclusion

From the results of the present study, it is concluded that, the adsorption process is a very effective process for the decolorization of wastewater, as we can reach 90% decolorization in few minutes. There is a need to enhance the adsorption process effectively by varying parameters, so as to bring down the values to permissible limits for wastewater before discharging it to the water environment. The removal of color from aqueous solutions and wastewaters using URS was studied by analyzing the effect of time and adsorbent dosage. Four types of isotherms were investigated, namely the Freundlich, Langmuir, Tempkin, and D–R isotherms. The correlation with these equations suggested the occurrence of monolayer adsorption onto a heterogeneous surface. Thermodynamic parameters such as standard enthalpy (ΔH°), standard entropy (ΔS°), and standard free energy (ΔG°) were determined. The negative value of ΔG° is -10.52×10^3 UPR at 303 K (30°C), indicating towards a spontaneous process. The positive value of ΔS° 46.39, showed the increased randomness at the solid-solution interface during adsorption and the positive value of ΔH°, 35.30×10^2 indicated the adsorption process was endothermic in nature.

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