Adsorption of Diclofenac Sodium from Aqueous Solution Using Polyaniline as a Potential Sorbent. I. Kinetic Studies

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Received 15 November 2009; accepted 11 February 2010
DOI 10.1002/app.32263
Published online 12 May 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: This study describes dynamic uptake of antibiotic drug diclofenac sodium from aqueous solution using polyaniline as sorbent. The sorbent polyaniline was prepared by oxidative polymerization of aniline and characterized by FTIR spectrum analysis and TGA. The optimum sorbent/sorbate mg/mL ratio and pH range for maximum drug uptake have been found to be 2.0 and 5.5 to 10.5, respectively. Out of various kinetic models applied, the pseudo second-order kinetic equation has been found to fit well on the kinetic uptake data. The pseudo second-order rate constants for adsorption have been found to be 0.982×10^{-2}, 7.24×10^{-2}, and 18.09×10^{-2} min^{-1} mg^{-1} g for drug solutions with initial concentrations of 10, 20, and 30 mg L^{-1}, respectively. The overall sorption process has been found to be governed by intraparticle diffusion.The sorptive removal of drug from aqueous solution has also resulted in enhancement in bacterial growth of *Escherichia coli*. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 3615–3622, 2010

Key words: polyaniline; adsorption; langmuir; antibiotics

INTRODUCTION

Antibiotics are probably the most successful family of drugs so far developed for improving human health.[1] In addition, they have also been frequently used for preventing and treating animals and plant infections, as well as for promoting growth in animal farming.[2] All these applications made antibiotics to be released in large amounts in natural ecosystems. In fact, most antibiotics used for preventing or treating infections in humans or animals as well as for promoting faster growth of livestock are only partially metabolized and are then discharged in the excreta, either to sewage treatment plants or straight forwarded in water or soils.[3] Besides, antimicrobial compounds used in intensive fish farming are added directly to the water rendering high local concentrations both in water and in adjoining sediments. In addition, antibiotics are topically added to the aerial organs of infected plants, although the amount of antibiotics used in plant agriculture is low as compared with human and veterinary medicine and animal production.[4] The overall result is that high concentrations of antibiotics are now detected in drinking waters, thus causing a decrease in the quality of water. These drugs possess a low biodegradability[5] and high toxicity,[6] and some are reported to be mutagenic and carcinogenic.[7] Hence, removal of these drugs from drinking water is essential and deserves due attention. It is noteworthy here that in Europe and US, the occurrence, behavior, and fate of pharmaceuticals have been investigated for river water, ground water, drinking water etc., and their concentrations have been detected in order of ng L^{-1} to μg L^{-1}.[8]

Conventional treatment systems, mainly based on the use of microorganisms have proven inadequate to effectively remove antibiotic drugs mainly because of their complex molecular structure.[9,10] Therefore, in recent past attempts have been made to remove antibiotics using other nonconventional techniques. These include Fenton process,[11,12] microscale membrane extraction,[13] removal by nanofiltration membrane,[14] molecular imprinting technique,[15] and adsorption.[16–19] Out of these, adsorption has proven to be an effective one as the pollutant can be removed in a wide range of concentrations.[20] Adsorption involves movement of adsorbate molecules in aqueous solution toward active sites in adsorbent pores, so it may be controlled by mass transfer effects and rate of adsorption on the active sites.[21] In this connection, we hereby report an investigation of adsorption of diclofenac sodium, an antibiotic drug onto polyaniline (PAn) sorbent. Recently,

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environmental chemists have focused their attention on conduction polymers like polyaniline, polypyrrole for recovery of heavy metals from aqueous solutions.[22] As PAn, in acid doped state (PAn/HCl) can be used as anion exchanger, it has potential to be used as sorbent for anionic drug like diclofenac sodium. This is a nonsteroidal active substance that acts as anti-inflammatory, with prolonged release, used in treatment of rheumatic disorders. The substance, 2-[(2,6-dichlorophenyl) amino] benzene acetic acid sodium salt (see Fig. 1) is a salt of a weak acid with a pKa of 4.0.

EXPERIMENTAL

Materials

Reagents aniline, hydrochloric acid, sodium hydroxide and ammonium persulphate were obtained from HiMedia chemicals, Mumbai, India and used as received except aniline, which was vacuum distilled before use. Nutrient agar and agar–agar Type-I were received from Merk (Mumbai, India). The double distilled water was used thoughout to prepare all solutions. The antibiotic drug diclofenac sodium (Molecular weight, 318.14; Molecular formula, $C_{14}H_{10}Cl_2NNaO_2$; Batch no., 93075K) was purchased from a local medical store.

Preparation of PAn

The sorbent PAn was prepared by oxidative polymerization of aniline, in aqueous medium, using potassium persulphate (KPS) as oxidant. In brief, 9 mL of aniline was dissolved into 90 mL of 1.0*M* HCl and the mixture was cooled to 4°C in an ice-bath. To this monomer solution, 270 mL of a pre-cooled 60.7 m*M* KPS solution (prepared in 1*M* HCl) was added slowly under vigorous stirring over a period of 30 min. As the reaction is highly exothermic ($\Delta H = 372$ kJ mol^{-1}), the reaction vessel was placed in an ice bath cooling system during addition of oxidant. After complete addition, the reaction mixture was left stirring for 3 h at low temperature. The precipitated powder (dark green in color) was filtered and washed sequentially with 180 mL of 1M HCl, 100 mL of 50% methanol and finally with double distilled water. The powder was dried in an electric oven (Tempstar, India) at 60°C for 6 h. Finally, the dried mass was grinded and passed through standard sieves to obtain particles with mean particle size of 185 μm.

FTIR spectral analysis

The FTIR (Fourier Transform Infrared) spectrum of PAn sorbent was recorded on FTIR spectrophotometer (Shimadzu, 8400S) using KBr.

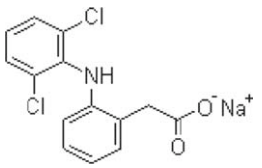

Figure 1 Structure of drug diclofenac sodium.

Adsorption experiments

Batch experiments were carried out by agitating a definite quantity of sorbent with 25 mL of drug solution of desired concentration in an Erlenmeyer flask of 100 mL capacity, under constant stirring speed in a thermostated flask shaker (Rivotek, India). The pH of the sorbate solution was maintained using 0.1*M* HCl or NaOH. After the adsorption was over, the solution was centrifuged and the supernatant was analyzed spectrophotometrically at 276 nm. The amount of drug adsorbed in mg per gram of sorbent (i.e., x/m) and percent sorption were calculated using following expressions:[21]

$$q_e \text{ i.e.} \frac{x}{m} = \frac{C_o - C_e}{W} V \quad (1)$$

$$\% \text{ Sorption} = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

where C_o is the initial concentration of drug solution (mg L^{-1}), C_e is equilibrium concentration of drug solution (mg L^{-1}), V is volume of solution (in liter) taken for adsorption experiment and W is amount of sorbent (in grams).

All the experiments were carried out in triplicate and average values have been reported in the data.

Antibacterial study

The biocidal action of drug Diclofenac Sodium was investigated using well method[23] against the gram-negative bacteria *E. coli.* The principle of this method is fairly simple. When an antibiotic is placed inside the well of suitable nutrient agar medium previously inoculated with the test bacterium, the antibiotic diffuses radically outward through the agar, producing antibiotic concentration gradient. The antibiotic is present at high concentration near the well and affects even minimally susceptible microorganisms. As the distance from the wells increases the antibiotic concentration drops, and only more susceptible pathogens are harmed. A clear zone or ring is present around an antibiotic well after incubation if the drug inhibits bacterial growth. The wider the zone surrounding a well the more susceptible the pathogen is.

For this, nutrient agar media was prepared and then sterilized by autoclaving it in conical flask for

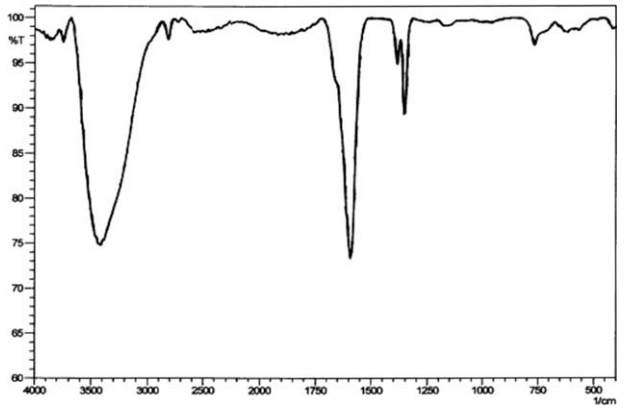

Figure 2 FTIR spectral analysis for plain polymer (PAn).

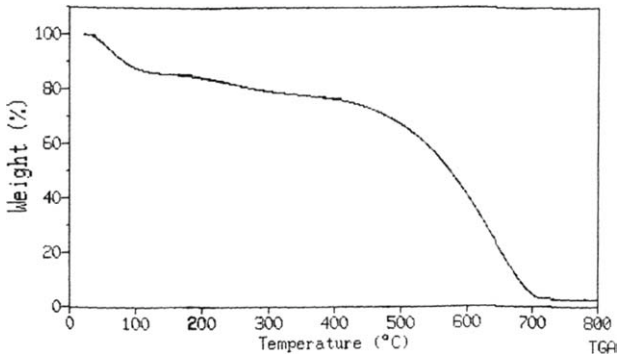

Figure 3 Thermo gravimetric analysis of plain polymer (PAn).

30 min. With this media, agar plates were prepared by transferring the media into sterilized petriplates. After solidification of the media, *E. coli* culture was spread on the solid surface of the media and then wells of diameter 70 mm were punched in it. To this inoculated Petridish l00 µl of drug solution was filled in the well and then incubated for 2 days at 37°C in the incubation chamber. The presence of inhibition zones containing bacterial culture around the well were observed. The diameters of each inhibition zone were measured in mm.

RESULTS AND DISCUSSION

FTIR spectral analysis

Characterization of plain polymer (PAn)

The FTIR spectrum of plain polymer (PAn) sample has been depicted in Figure 2.

Figure 2 shows a prominent peak at 3381 cm^{-1} corresponding to N—H stretching of secondary amine. A peak obtained at the range 2810 cm^{-1} is due to symmetrical $>CH_2$ stretching of alkanes. N—H bending vibration and C—N stretching vibration of aromatic secondary amine appears at 1515 cm^{-1} and 1350 cm^{-1}, respectively.

TGA analysis

The thermogram of PAn has been shown in Figure 3. The curve obtained reveals that the initial weight loss of polymer in the range of ambient to 80°C is due to the loss of moisture that was bound to the polymer. Later on, the initial decomposition takes place at about 170°C (i.e. T_{id}) and the final decomposition temperature, T_{fd}, is almost 410°C. Therefore, it is quite clear that PAn exhibits fair thermal stability up to 170°C.

Effect of sorbent/sorbate (mg/mL) ratio on drug uptake

To optimize the drug uptake conditions, various quantities of sorbent (in mg) were agitated with 25 mL drug solution of initial concentration 10 mg L^{-1} at 28°C for a period of 1 hr. The percent drug uptake was plotted against sorbent/sorbate (mg/mL) ratio as shown in Figure 4. It is quite clear that as the mg/mL ratio increases, drug sorption also increases and finally attains a maximal value of nearly 90% when the sorbent/sorbate ratio becomes 2.0. Therefore, in all the sorption experiments the sorption was carried out with 50 mg of sorbent in 25 mL drug solution of desired concentration. The above finding many simply be attributed to the fact that initially the increase in sorbent dose cause an enhancement in number of active sites available on sorbent surface for drug uptake per unit volume of sorbate solution. However, later on there comes a stage when nearly all the active sites available have been occupied and therefore percent sorption attains an optimal value.

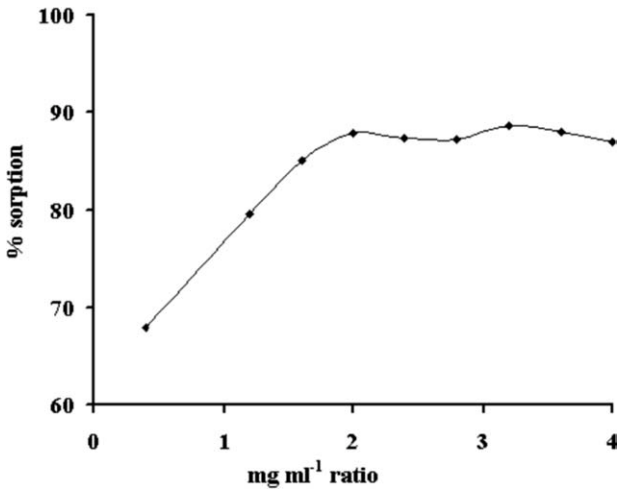

Figure 4 Effect of solid/liquid ratio on the drug uptake.

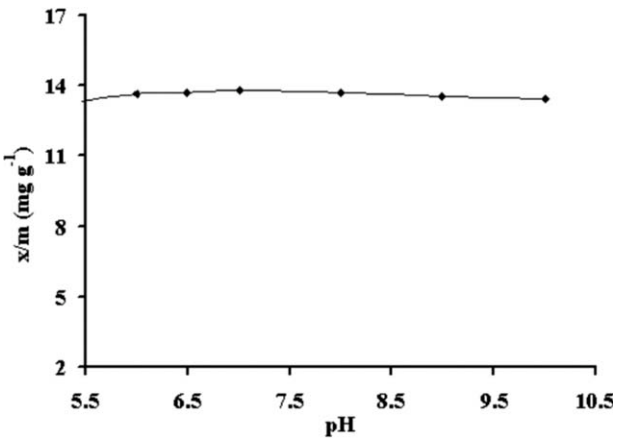

Figure 5 Effect of pH on drug uptake.

Effect of pH

pH of sorption system (i.e. sorption plus sorbate) plays a significant role in governing the extent of sorption. The solubility of drug diclofenac sodium, in the pH range of 1.0 to 4.5, is almost between 1.2 to 3.6 mg/L, and therefore for the study of pH effect on drug uptake, solutions with final concentrations of 10 mg L^{-1} were prepared in the range of 5.5 to 10.5 and adsoption experiments were carried out at 28°C. The results, as depicted in Figure 5, indicate that the drug uptake remains almost the same (i.e., 13.48–13.71) in the whole pH range studied. The observed findings may be explained as follows. In the range of 4.5–6.5 the aniline used was acid doped (PAn/HCl) thus exhibiting fair capacity to undergo anion exchange with anionic drug molecules. However, when pH of the sorbate solution is raised by adding NaOH, it changes into undoped form, thus possessing free amine or imine groups in the polymer.[24] In this case, heteroatoms, such as O and Cl, present is in drug molecule may interact with —H atoms of emeraldine base (EB) form of PAn. In this way variation in pH of the sorbate solution does not cause any appreciable change in amount of drug adsorbed. Therefore, sorptive removal can be carried out at any pH value of sorbate solution, in the overall range of 5.5 to 10.5.

Kinetic studies

Effect of drug concentration and contact time

The initial concentration of adsorbate in the solution provides an important driving force in overcoming the mass transfer resistance between the aqueous and solid phases.[25] In addition, it has also been shown that the rate of adsorption on the surface should be proportional to a driving force times on area.[26] The effect of initial drug concentrations and contact time are illustrated in Figure 6. It appears that more drug is retained by the sorbent, and the adsorption mechanism becomes more efficient, as the initial drug concentration increases. For the initial concentration at 10, 20, and 30 mg L^{-1}, the equilibrium uptake capacities were found to be 13.50, 28.10, and 43.146 mg g^{-1}, respectively. A close look at the Figure 6 also reveals that in all the three solutions, the initial drug uptake was fast and practically it required nearly 20, 10, and 8 min for adsorption of most of the (i.e., >90%) drug. Therefore, fast uptake of drug molecules is due to solute transfer, as there are only sorbent–sorbate interactions with negligible interference from solute–solute interactions. The initial rate of adsorption was therefore greater for high initial drug concentration because of increase in mass transfer driving force which diminished the resistance to the drug uptake. Similar types of results have also been reported elsewhere.[25]

Kinetic models

To investigate mechanism of diclofenac sodium adsorption and potential rate-controlling steps, such as mass transport and diffusion through pores, various kinetic models were used to test experimental data. These kinetic models include pseudo first-order equation, pseudo second-order equation, Simple Elovich model, and intraparticle diffusion models.[26]

Pseudo first-order kinetic model

The sorption kinetics can be described by pseudo first-order equation as suggested by Lagergren.[27]

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{3}$$

where k_1 (min^{-1}) is the rate constant of pseudo first-order sorption, q_t (mg g^{-1}) denotes amount of sorbate

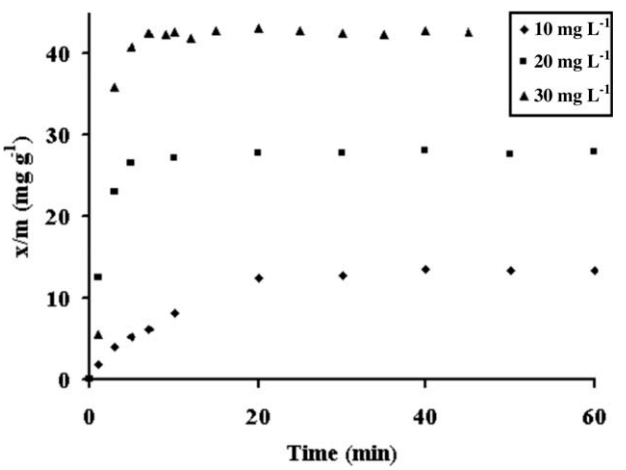

Figure 6 Kinetics of adsorption of drug onto polymeric sorbent at 28°C.

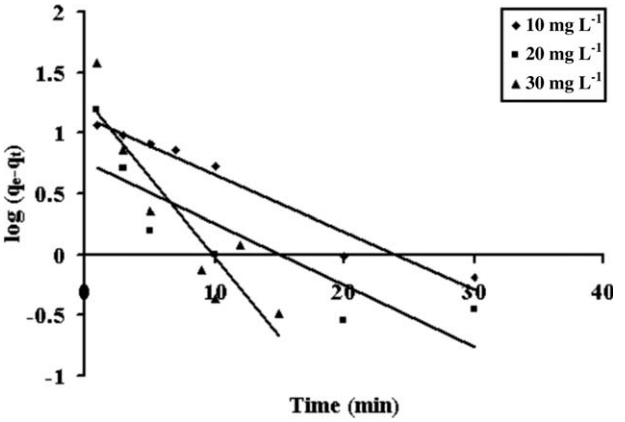

Figure 7 Pseudo first-order kinetic plots for sorption of diclofenac sodium onto polymeric sorbent at 28°C.

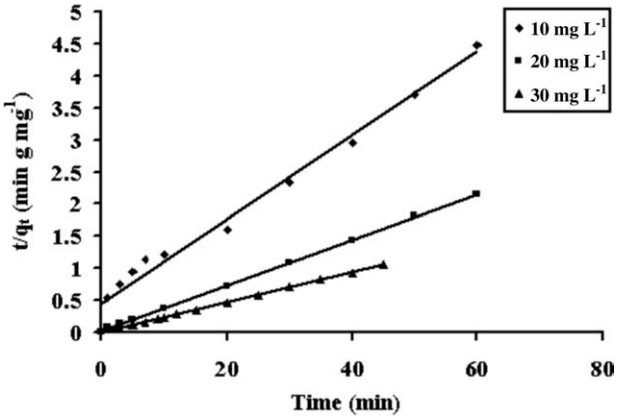

Figure 8 Pseudo second-order kinetic plot for sorption of drug diclofenac Sodium onto polymeric sorbent at 28°C.

adsorbed at time t, q_e (mg g^{-1}) the adsorption capacity in equilibrium and t (min) is the time. After definite integration by applying boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, the above equation becomes

$$\log (q_e - q_t) = \log q_e - \frac{k_1 \cdot t}{2.303} \tag{4}$$

Values of parameters k_1 and q_e are obtained using slope and intercepts of the linear plot obtained between log $(q_e - q_t)$ and t.

Pseudo second-order kinetic model

The pseudo second-order kinetic model, developed by Ho and McKay[28] can be given as

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{5}$$

where k_2 (g mg^{-1} min^{-1}) is the rate constant of the pseudo second-order. Definite integration of eq. (5) for boundary conditions $q_t = 0$ when $t = 0$ and $q_t = t$ when $t = t$, the following equation may be obtained:

$$\frac{t}{q_t} = \frac{1}{(k_2 q_e^2)} + \left(\frac{1}{q_e}\right) \cdot t \tag{6}$$

The values of initial sorption rate constant, h (mg/g min), at $t = 0$ can be defined as

$$h = k_2 \cdot q_e^2$$

The values of initial sorption rate (h), the equilibrium sorption capacity (q_e) and the pseudo second-order rate constant k_2 can be obtained using slopes and intercept of linear plot of t/q_t against t.

Simple Elovich model

This equation, first proposed by Roginsky and Zeldovich in 1934, and now generally known as Elovich equation has been extensively applied to biosorption data.[29] The Elovich equation is given as follows:

$$\frac{dq_t}{dt} = \alpha\, e^{-\beta q_t} \tag{7}$$

where α is the initial rate (mg g^{-1} min^{-1}), and the parameter β is related to the extent of surface coverage and extent of activation energy for chemisorption. The integrated form of eq. (7) is

$$q_t = \alpha' + \beta' \{\ln t \tag{8}$$

α' and β' can be evaluated using slope and intercept of linear plot obtained between q_t and lnt.

The above three models, namely pseudo first-order equation, pseudo second-order equation and Elovich equation have been well illustrated in Figures 7, 8, and 9 respectively for drug uptake from sorbate solutions with initial concentrations of 10,

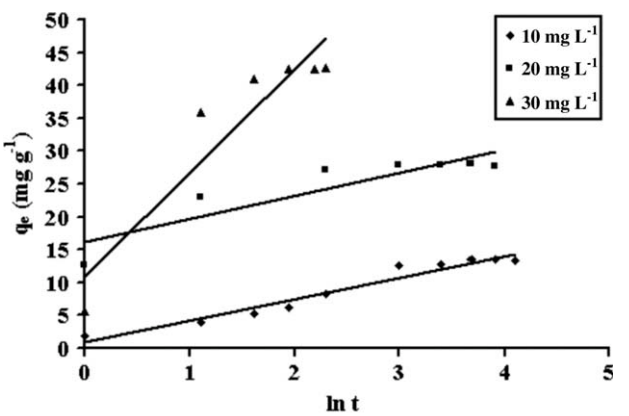

Figure 9 Simple Elovich model for sorption of drug diclofenac sodium onto polymeric sorbent at 28°C.

TABLE I
Parameters for Pseudo First-Order, Pseudo Second-Order, and Simple Elovich Kinetic Models obtained Using Uptake Data at 28°C

	Pseudo first-order			Pseudo second-order			Simple Elovich Model			
Conc. (mg L^{-1})	R^2	K_1 (min^{-1})	q_e (mg g^{-1})	R^2	K_2(min^{-1} mg^{-1} g)	q_e (mg g^{-1})	R^2	α'	β'	$q_{e\ exp}$ (mg g^{-1})
10	0.961	10.94×10^{-2}	13.645	0.982	0.982×10^{-2}	15.244	0.995	0.8952	3.290	13.506
20	0.739	11.7×10^{-2}	5.875	0.999	7.24×10^{-2}	28.169	0.807	16.073	3.529	28.101
30	0.81	30.23×10^{-2}	19.980	0.999	18.09×10^{-2}	42.918	0.869	10.948	15.772	43.146

20, and 30 mg L^{-1} at 28°C. The various parameters aforementioned have been given in Table I. The regression value, obtained for the three models, clearly suggests that the order of fitness of these models is: pseudo second order > Elovich model > pseudo first order. The data given also reveals that the graphical values of equilibrium adsorption capacity, i.e., q_e are in close agreement with the experimentally obtained values for pseudo second-order kinetic model only.

External diffusion sorption model

If sufficient agitation is provided during the sorption process, then it may be possible to avoid bulk diffusion and hence it can be assumed that rate is not limited by mass transfer from the bulk liquid to the surface of the sorbent particle. Under such circumstances, diffusion from the film to the surface of the adsorbent, also called external diffusion, may govern the sorption process. In the case of strict surface adsorption, the variation in the adsorption rate should be proportional to the first power of the concentration. However, when pore diffusion limits the sorption process, the relationship between initial solute concentration and rate of adsorption remains no longer linear.

In this study, the Spahn and Schlunder[30] model was chosen to describe external diffusion on the sorbent:

$$\ln \frac{C_t}{C_0} = -k_s \frac{A}{V} t \tag{9}$$

where C_0 and C_t are the drug solutions concentrations (mg L^{-1}) at time $t = 0$, and at time t respectively; t is the time (min), k_s represent external mass transfer coefficient (m min^{-1}), V is the volume of the equilibrating solution (l), and A indicates the surface area (m^2 g^{-1}) of sorbent.

To apply this model, the dynamic uptake data obtained for drug solution with initial concentration of 10 mg L^{-1} was selected and ln C_t/C_0 values were plotted against t as illustrated in Figure 10. The plot obtained was quite linear with a regression value of 0.9451. The external mass transfer coefficient k_s, calculated using slope and intercept, was found to be -1.5×10^{-6} m min^{-1}.

Intraparticle diffusion

The adsorbate transport from the solution phase to the surface of the adsorbent particles occurs in three steps, viz. film diffusion, pore diffusion and intraparticle transport. The slowest of the three steps controls the overall rate of the process. Generally, pore diffusion and intraparticle diffusion are often rate limiting steps in a batch reactor, whereas for a continuous flow system film diffusion is more likely to be the limiting step.[31] The adsorption rate parameter that controls the process for most of the contact time is the intraparticle diffusion.[32] The possibilibity of intraparticle diffusion resistance affecting was explored by using the intraparticle diffusion model, as:[33]

$$q_t = k_{id} t^{1/2} + I \tag{10}$$

where k_{id} is the intraparticle diffusion rate constant. According to eq. (10), a plot of q_t versus $t^{1/2}$ should be a straight line with a slope k_{id} and intercept I when adsorption mechanism follows the intraparticle diffusion process. Value of intercept gives an idea about the thickness of boundary layer i.e., the larger the intercept; the greater will be boundary layer effect.[34] The dynamic drug uptake data, displayed in Figure 6 was used to draw q_t versus $t^{1/2}$ plots for the sorbate solutions with initial concentration of 10, 20, and 30 mg L^{-1} (see Fig. 11). It is clear

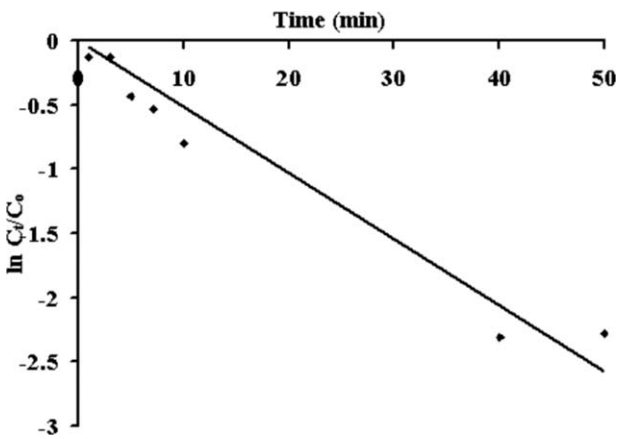

Figure 10 ln C_0/C_t plots for calculation of external mass transfer coefficient from external diffusion sorption model.

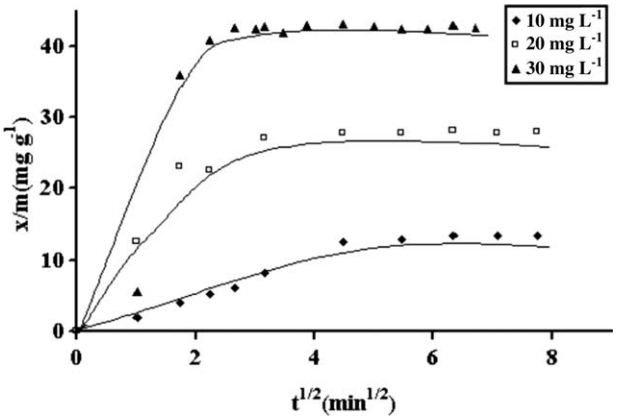

Figure 11 q_t versus $t^{1/2}$ plots for calculation of rate constant for intraparticle diffusion.

that the plots do not pass through the origin, and are biphasic in nature. The deviation of straight lines from the origin may be due to the difference between the rates of mass transfer in the initial and final steps of adsorption. In addition, the deviation also indicates that pore diffusion is not the sole rate-controlling step.[35] From the Figure 11 it may be seen that there are two separate regions, the first portion is attributed to the bulk diffusion and the second portion to the intraparticle diffusion. The values of $k_{id,1}$ and $k_{id,2}$ as obtained from the slopes of the two linear parts have been given in the Table II.

Antibacterial test

One of the main disadvantages of presence of antibiotic drugs in water bodies is that they kill microorganisms, such as bacteria, fungi, actinomycetes,[36,37] which take up heavy metal ions and thus help to protect the aquatic system. In this way, presence of antibiotic drugs causes metal ion pollution to increase by reducing the growth of microorganisms. To test this 25 mL drug solution with concentration of 250 mg L^{-1} was agitated with precalculated quantity of drug and the solution, obtained after adsorption was used to inhibit bacterial growth in petridishes as described in the experimental section. The results, as illustrated in Figure 12, indicate that after adsorption the remaining solution is less effective in causing the bacterial death thus showing more growth of bacterial colonies indicated by the relatively smaller radius of zone of inhibition.

TABLE II
Intraparticle Diffusion coefficients obtained for Diffusion of Drug molecules in solutions with Initial concentrations of 10, 20, and 30 mg L^{-1} at 28°C

Initial concentration (mg L^{-1})	$K_{id,1}$ (mg mg^{-1} $min^{-1/2}$)	$K_{id,2}$ (mg mg^{-1} $min^{-1/2}$)
10	2.4251	22.73×10^{-2}
20	11.418	83.29×10^{-2}
30	15.21	204.4×10^{-2}

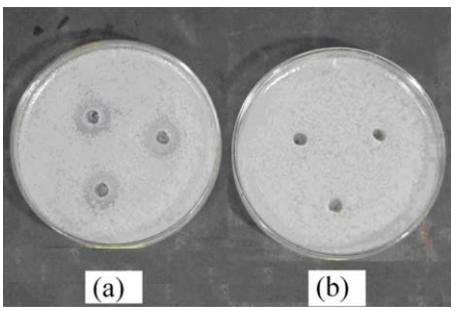

Figure 12 Antibacterial test: (a) Showing clear zone of inhibition before adsorption of drug DS. (b) Showing smaller zone of inhibition after adsorption of drug DS. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

CONCLUSIONS

From the above study it may be concluded that PAn acts as efficient sorbent for the removal of antibiotics drug diclofenac sodium from wastewater. It is effective over a wide range of pH and the dynamic sorption process is best interpreted in terms of pseudo second-order kinetic model. In addition, the intraparticle diffusion, along with other mechanism, is involved in overall drug uptake. The removal of drug from water enhances the bacterial growth which may be beneficial in removing heavy metal ions.

The authors are thankful to Dr. O. P. Sharma, Head of Department for his unconditional and kind support.

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