Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Poly(acrylamide-co-itaconic acid) as a Potential Ion-Exchange Sorbent for Effective Removal of Antibiotic Drug-Ciprofloxacin from Aqueous Solution

S. K. Bajpai[a]; Mousumi Bhowmik[a]
[a] Polymer Research Laboratory, Department of Chemistry, Govt. Model Science College (Autonomous), Jabalpur, India

Online publication date: 29 December 2010

To cite this Article Bajpai, S. K. and Bhowmik, Mousumi(2011) 'Poly(acrylamide-co-itaconic acid) as a Potential Ion-Exchange Sorbent for Effective Removal of Antibiotic Drug-Ciprofloxacin from Aqueous Solution', Journal of Macromolecular Science, Part A, 48: 2, 108 — 118
To link to this Article: DOI: 10.1080/10601325.2011.534718
URL: http://dx.doi.org/10.1080/10601325.2011.534718

Journal of Macromolecular Science, Part A: Pure and Applied Chemistry (2011) **48**, 108–118

ISSN: 1060-1325 print / 1520-5738 online
DOI: 10.1080/10601325.2011.534718

Taylor & Francis
Taylor & Francis Group

Poly(acrylamide-co-itaconic acid) as a Potential Ion-Exchange Sorbent for Effective Removal of Antibiotic Drug-Ciprofloxacin from Aqueous Solution

S. K. BAJPAI* and MOUSUMI BHOWMIK

Polymer Research Laboratory, Department of Chemistry, Govt. Model Science College (Autonomous), Jabalpur, India

Received June 2010, Accepted August 2010

This study describes equilibrium and kinetic sorption studies to remove the antibiotic drug Ciprofloxacin (CF) from aqueous solutions using poly(acrylamide-co-itaconic acid) [poly(AAm-co-IA)] as polymeric cation exchanger sorbent material. The co-polymeric sorbent was prepared by free radical induced aqueous polymerization and was characterized by FTIR spectroscopy and TGA analysis. In addition, its physicochemical parameters were also determined. The various isotherm models, when applied to equilibrium sorption data at 28°C, followed the following order: Langmuir > Temkin > Freundlich, with the fair maximum sorption capacity (Q_o) of 178.5 mg g^{-1}. The kinetic sorption data, obtained at 28°C, was applied to kinetic models such as pseudo first order equation, pseudo second order model and a simple Elovich model. Based on regression values , the order of fitness of these models was pseudo second order > pseudo first order > simple Elovich model. The second order adsorption coefficients k_{2ads}were found to be 58×10^{-3}, 52.7×10^{-3}, 34.01×10^{-3} g/mg min for drug solutions with initial concentrations of 10, 20 and 30 mg L^{-1} respectively The sorption mean free energy from the Dubinin–Raduschkevich (DR) isotherm was found to be nearly 8.839 kJ mol^{-1} indicating an ion-exchange mechanism for drug uptake. The optimum pH value of sorbate solution for drug uptake was found to be around 6.0. Finally, the antibacterial action of drug was investigated and it was found that after adsorption there was a decrease in bacterial growth inhibition efficiency of drug solution.

Keywords: Antibiotic drugs, Langmuir, adsorption, toxicity, ion-exchange resin

1 Introduction

Antibiotics are widely used in human and veterinary medicines for therapeutic purpose. They are also largely used in animal operations for growth promotions and for disease prophylaxis (1). They are often partially metabolized after administration and a significant portion of the antibiotic can be excreted as the parent compound or in conjugated forms that can be converted back to the parent antibiotic. These residual antibiotics from human and animal can enter the environment via various pathways, such as wastewater effluent discharge, runoff from land to which agricultural or human waste has been applied and leaching. In fact, it is widely accepted that wastewater treatment plants (WWTPS) are the main entry point of urban antibiotics in the aquatic environment.

Recently, there has been growing concern on this potential water pollution problem caused by antibiotics. Different from conventional pollutants, these materials which are discharged daily, have high polarity and are easily soluble in water. So there are greater chances of their accumulation in aqueous environment such as sea, river, ponds etc. and thus, their chronic influence over human beings are of much concern (2, 3). In addition, their presence in water may cause the death of micro-organisms which are effective in wastewater treatment (3). A variety of antibiotics have been detected in waste effluents and natural waters at ng/L to low μg/L levels (4). Antibiotics can remain in the tissues of animals, so that they can be considered as food pollutants. It has been suggested that these compounds might trigger allergic reactions on occasion, and contribute to select for antibiotic-resistant bacteria in the human microbiota (5). In addition, antibiotics released to soils or waters can modify the local environmental microbiota, producing changes in their composition or activity that are not fully understood. The alterations in the bacterial populations include selection of resistant mutants in susceptible species, changes in the distribution of antibiotic resistance genes

*Address correspondence to S. K. Bajpai, Polymer Research Laboratory, Department of Chemistry, Govt. Model Science College (Autonomous), Jabalpur (M.P.) 482001, India. E-mail: polymerlab@rediffmail.com; sunil.mnlbpi@gmail.com

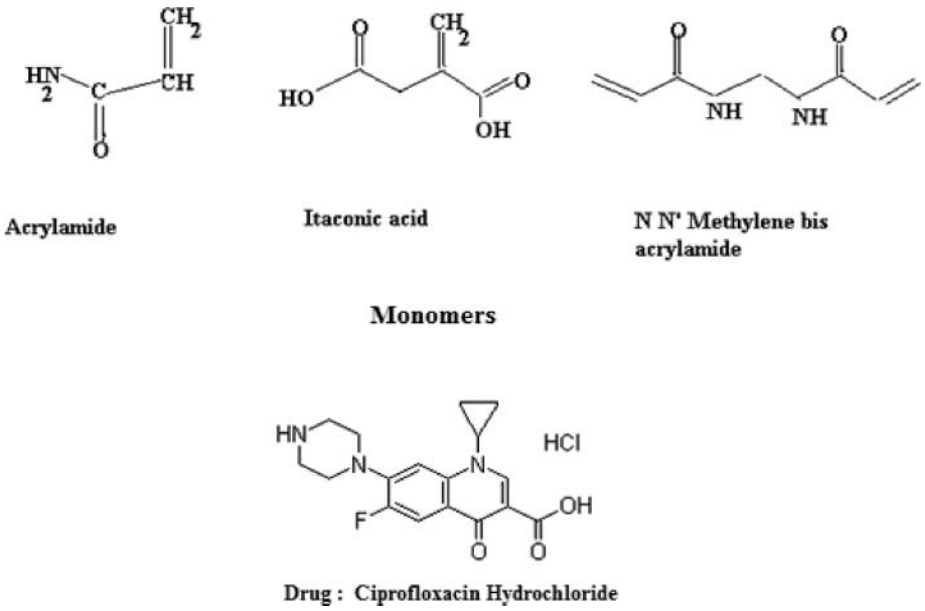

Fig. 1. Structures of monomers and drug.

present in gene-transfer units, and selection of resistant species in such a way that overall composition of microbiota is modified. For example, exposition to the ciprofloxacin of salt marsh sediment microbial communities favors selection of sulphate-reducing and Gram-negative bacteria (6). Apart from this consequence of antibiotic pollution, antibiotics can also produce transient changes in the activity of microbial populations that might be relevant for their productivity even at their sub-inhibitory concentration. It has been described that the pollution of manure with silfatdiazine reduces microbial activity, mainly some processes in nitrogen turnover, besides increasing resistance in soil (7). Recently, Kummerer (8) has reviewed the effect of antibiotics in the environment.

There are many methods that have been employed in the recent past for the removal of antibiotics from water sources which include use of nanofiltration membrane (9), coagulation(10), membrane bioreactor (12), nanoscale iron particles (13), activated carbon (14), bentonite clay (15), polysaccharide (16) etc. In the recent past, a number of polymeric sorbents have been employed for the purpose of removing antibiotic drugs from aqueous solutions. For example, Pisarev et al. (17) have studied sorption of antibiotic erythromycin using a copolymer of methacrylic acid and ethylene glycol dimethacrylate. Similarly a copolymer of methacrylic acid and n-vinyl-2-pyrrolidone has been used as an imprinting polymer for effective and selective removal of antibiotic sulfamethoxazole (18). The removal efficiency was found to be nearly 90%. Similarly, polyaniline has been exploited for effective removal of diclofenac sodium from aqueous solution (19). The overall sorption mechanism was found to be diffusion controlled. Apart from synthetic polymers, natural polymers like pectin have been used in the form of beads to remove ciprofloxacin (20).

In the present work, we have made a fair attempt to use copolymeric ion exchange sorbent for removal of antibiotic drug Ciprofloxacin (CF) from aqueous solutions. The drug Ciprofloxacin (Fig. 1) is a broad spectrum antibiotic that is active against both Gram positive and Gram negative bacteria (21). It destroys micro-organisms by interfering with their DNA gyrase, a type II bacterial topoisomerase necessary for DNA synthesis (22).

2 Experimental

2.1 Materials

Monomers acrylamide (AAm), and itaconic acid (IA), crosslinker N,N′methylene bisacrylamide (MB) (Fig. 1) and initiator potassium persulphate (KPS) were purchased from Hi Media Chemicals, Mumbai, India ,and were used as received except AAm which was recrystallized in methanol to remove the inhibitor. The model drug Ciprofloxacin (CF) (molecular weight 367.80, formula $C_{17}H_{18}FN_3O_3.HCl$, Batch no.CFP-007) was obtained from Karnataka Antibiotics Pharmaceuticals Limited (A Govt. of India Enterprise). The aqueous solution of drug was used throughout the investigations.

2.2 Preparation of Poly(AAm-co-IA) Sorbent

The copolymeric sorbent was prepared by carrying out free-radical induced aqueous polymerization of AAm and IA, using MB as crosslinker and KPS as initiator (23). In brief, 211.1 mM of monomer AAm, 7.6 mM of IA, and 6.4 mM of MB as crosslinker was dissolved in water and the final volume was made up to 75 ml. Finally, 3.7 mM of KPS

was added and the reaction mixture was put in an electric oven (Tempstar, India) at 60°C for a period of 2 h. The copolymer formed was equilibrated in water for 48 h to remove unreacted salts and then dried at 40°C in a dust-free chamber. Finally, the dried mass was ground and passed through standard sieves to get particles with mean particle size of 421μm.

2.3 Characterization of Sorbent

2.3.1. *Physicochemical Parameters*

The copolymeric sorbent was analyzed for measurement of its physicochemical parameters. The method of determination was adopted from our previous report (24) using n-heptane as a non-sorbent.

2.3.2. *Thermogravimetric Analysis of Co-polymeric Sorbent*

The TGA was performed in Indian Institute of Technology, Mumbai, India, using thermogravimetric analyzer (Perkin Elmer Thermal Analyzer). About 12.0 mg of powdered copolymeric sorbent was placed in ceramic crucible and analyzed over the temperature range from 25°C to 800°C at the rate 10°C min^{-1}under a dry flow of nitrogen at the rate of 50 ml min^{-1}.

2.3.3. *FTIR Spectral Analysis*

The FTIR (Fourier Transform Infrared) spectrum of co-polymeric sorbent [poly(AAm-co-IA)] was recorded on FTIR spectrophotometer (Shimadzu, 8400S) using KBr.

2.4 Adsorption Experiments

Sorption studies were carried out in thermostated water bath shaker (Rivotek, India) at 28°C, with a shaking speed of 200 rpm using Erlenmeyer flasks of 100 ml capacity. Batch experiments were performed by equilibrating 0.02 g of adsorbent with 50 ml of drug aqueous solution of pre-determined concentrations. The required pH was obtained by adding a few drops of 0.1 M HCl or 0.1 M NaOH. The sorption system was agitated at 200 rpm for a period of 1 h and was centrifuged and the supernatant was analyzed spectrophotometrically (Systronics 2201-UV-spectrophotometer) at 273 nm. The amounts of drug adsorbed q_e, in mg per g of sorbent and percent sorption were determined using following equations (25).

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

and

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

Where $C_o$and C_e are initial and final concentrations of drug solutions (mg L^{-1}), respectively; and V and W are the volume of sorbate solution study (in liter) and the amount of sorbent used (in g), respectively. The concentrations of drug in the solutions were estimated using Lambert-Beers-Law plotted for drug solutions of known concentrations.

All the experiments were carried out in triplicate and average values have been reported in the data with standard duration of 2%. In the experiments, where higher deviation was observed, the data was discarded and a new experiment was conducted.

2.5 Antibacterial Study

The effect of drug (CF) adsorption on its antibacterial action was investigated on *E. coli* using a well method (26). This is based on the principle that when the drug is placed inside the well of a suitable nutrient agar medium inoculated with test bacterium, there is radial diffusion of drug outwards through the agar, thus creating an antibiotic concentration gradient. The concentration of drug is nearer the well, and decreases on moving outwards. Finally, an inhibition zone is produced around the antibiotic well, whose width is a measure of susceptibility of pathogens.

For this nutrient, agar media was prepared and then sterilized by autoclaving it in a conical flask for 30 min. With this media, agar plates were prepared by transferring the media to these sterilized Petri plates. 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. To this inoculated Petri dish, 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.

3 Results and Discussion

3.1 Characterization of Sorbent

3.1.1. *Physicochemical Parameters*

Table 1 describes the physicochemical parameters of synthesized copolymeric sorbent. Here, it is interesting to see that, the % porosity is around 67% which suggests not only the porous nature of the sorbent, but also the possibility of occurrence of intraparticle diffusion phenomenon.

Table 1. Various physical parameters obtained for copolymeric sorbent

S.No.	*Parameters*	*Values*
1.	Pore volume	2.0 mL/g
2.	Percent porosity	66.67 %
3.	True density	1.0 mL/g
4.	Bulk density	0.33 mL/g

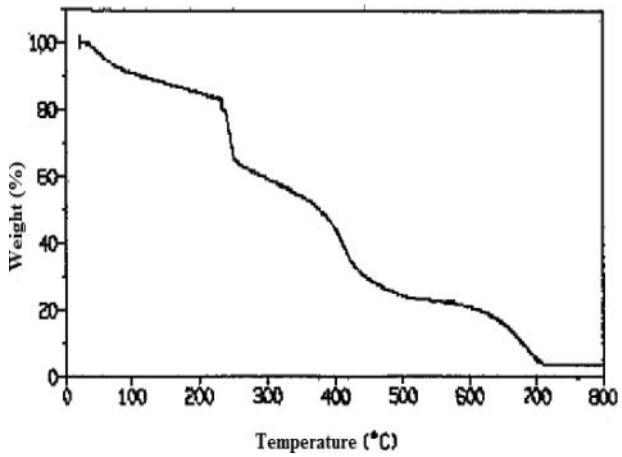

Fig. 2. Thermogravimetric analysis of co-polymer [poly(AAm-co-IA)].

3.1.2. *Thermogravimetric Analysis of Copolymeric Sorbent*

The thermogravimetry analysis of copolymeric sorbent poly(AAm-co-IA) was performed to investigate its thermal stability. The results, as depicted in Figure 2 shows that the initial decomposition temperature (T_{id}) is nearly 210°C, while the final decomposition temperature T_{fd} is approximately 570°C. This suggests that the polymer is fairly stable up to 200°C.

3.1.3. *FTIR Spectral Analysis*

The FTIR spectra of plane copolymeric sorbent [poly(acrylamide-co-itaconic acid)], as depicted in Figure 3, clearly indicates a narrow band appeared at 3190 cm^{-1}, due to the overlapping of O-H and N-H stretching of acid and amide, respectively. The symmetric and asymmetric $>CH_2$ stretching of methylene occurs near 2930 and 2856 cm^{-1}, respectively. A prominent peak at 1650 cm^{-1}corresponds to $>C{=}O$ stretching vibration of amide. Another band arising for C-O stretching appears near about 1325 cm^{-1}.

3.2 Effects of Sorbent/Sorbate Ratio (mg/mL) on Drug Uptake

In order to optimize the sorption experimental conditions, different quantities of sorbent were added to 50 ml of sorbate solutions with an initial concentration of 20 mg L^{-1}, to give a wide range of sorbent/sorbate ratio from 0.4 to 4.0. The results, as depicted in Figure 4, clearly reveal that as the value of sorbent/sorbate ratio increases, the amount of drug adsorbed per gram of sorbent decreases. This may be explained on the basis of the fact that initially the amount of sorbent present in 50 ml of sorbate solution (say 20 mg of sorbent in 50 ml of sorbate to give a ratio of 0.4) is more than enough to cause an effective uptake of molecules to yield a higher drug uptake of 15.5 mg g^{-1}. However, as the amount of sorbent is increased, the number of active

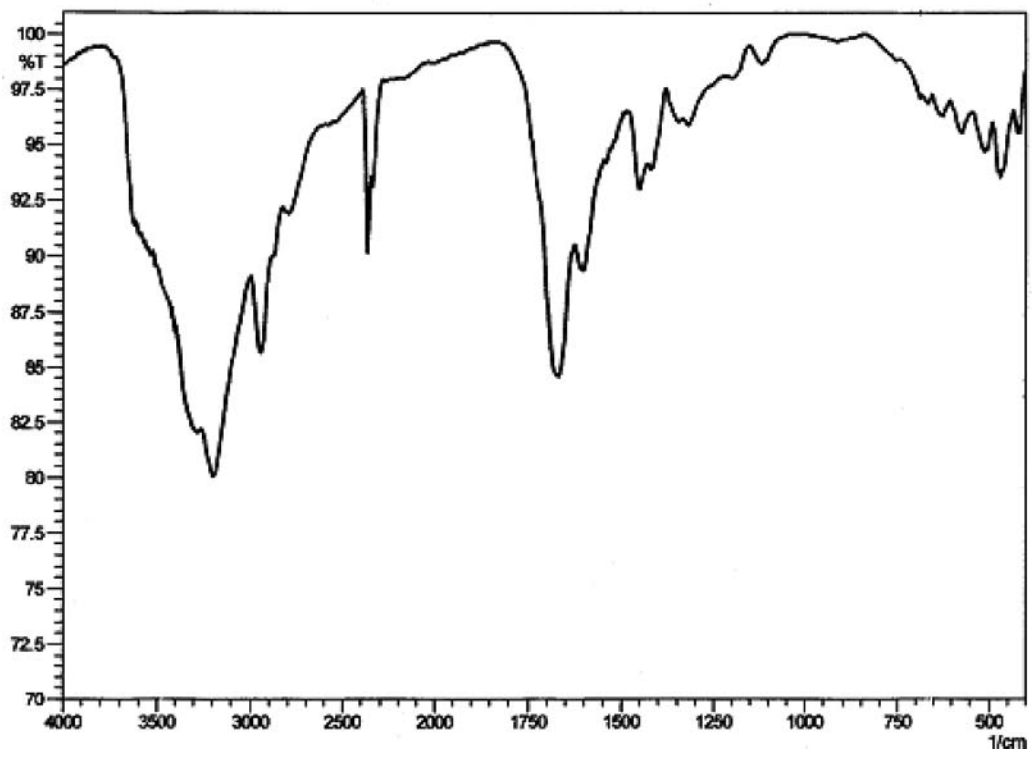

Fig. 3. FTIR spectral analysis of co-polymeric sorbent [poly(AAm-co-IA)].

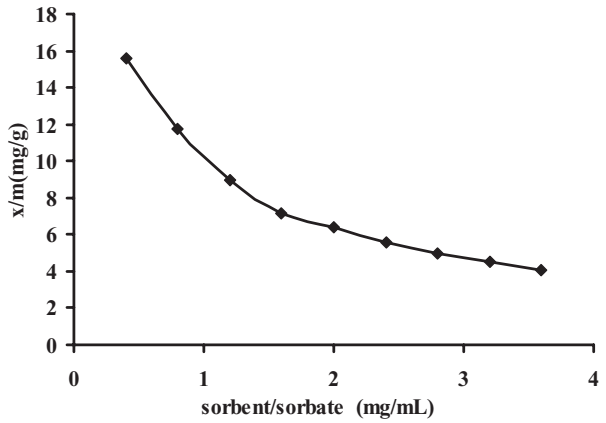

Fig. 4. Effect of solid/liquid ratio on the drug uptake.

sites available for sorption also increases, but there is not a sufficient number of drug molecules available for sorption on these new available sites. In other words, the amount of sorbent is increased in a greater proportion, while drug uptake increases slightly due to the unavailability of drug molecules for accommodation at newly available sorption sites. Therefore, the x/m value (i.e., drug adsorbed in mg per g of sorbent) continues to decrease with an increase in sorbent amount. Hence, in order to obtain maximum drug uptake at the cost of a minimum quantity of polymeric sorbent, a sorbent/sorbate ratio of 0.4 (i.e., 20 mg of sorbent in 50 ml of drug solution) was selected to carry out adsorption experiments in the present study.

3.3 Effect of pH on Drug Sorption

pH of a sorption system plays a significant role in affecting the extent of adsorption, particularly when both sorbent and sorbate molecules are ionic in nature (27). In the present study, both poly(AAm-co-IA), the sorbent and ciprofloxacin, the sorbate are ionic in nature and therefore,

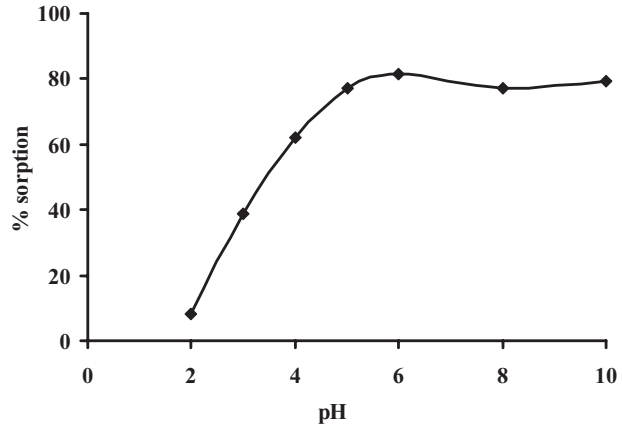

Fig. 5. Effect of pH of the drug solutions on the amount of drug sorbed.

pH of the sorption system was expected to play a significant role in obtaining optimum drug adsorption. In order to investigate this, a drug solution of a known concentration was prepared in the pH range of 2.0 to 10.0 and agitated with a definite quantity of sorbent at 28°C. The plot drawn between percent sorption and corresponding pH of the solutions has been depicted in Figure 5. It can clearly be seen that percent drug uptake increases with pH of the solution and attains almost saturation value in the pH range of 6 to10. The observed findings may be explained as below.

When pH of the sorbate solution is 6.0, the copolymeric chains of sorbent particles remain in ionized state due to complete ionization of –COOH groups of itaconic acid present within the copolymeric network. Therefore, ionized drug molecules present in sorbate solution undergoes exchange with free H^+ ions present within the sorbent particles. Due to this ion-exchange process, ionized drug molecules enter into polymer network of sorbent and bind firmly with residual $–COO^-$ groups via electrostatic force of attraction. In addition, the fully swollen network of sorbent particles also enhances the diffusion of drug ions into network (28). As a result of these two factors, a maximum uptake of nearly 81% is obtained. Here, it is also to be noted that Ciprofloxacin is an antibiotic drug with pk_a values in the range of 5.1 to 6.8 .Therefore, at the sorbate solution pH of 6.0,it is almost in the ionized form (29) which also favors its sorption through ion-exchange process. However, when pH of the sorbate solution is below 6.0 the drug uptake is also found to decrease. The reason is that as the pH of the solution is 5.0, it is below the pK_2 value of itaconic acid (i.e., 5.44) (30) and hence, some carboxylic groups of copolymeric sorbent become unionized thus causing a decrease in the extent of ion-exchange process; as a result, drug uptake decreases. When pH of the sorbate solution is further lowered to 3.0, it is just below the first pK_avalue of itaconic acid (i.e., 3.85) and therefore, all carboxylic groups of itaconic acid, present within the copolymeric sorbent, remain unionized thus imparting almost neutral character to the sorbent gel particles. As a result, ion exchange process is now no longer operative and hence the extent of sorption becomes quite low (i.e., nearly 35%). Finally, when pH of the system is 2.0, almost minimum 8% drug sorption is observed. This is due to the fact that, at an appreciably lower pH, polymeric gel particles acquire a completely non-ionic nature due to the presence of unionized carboxylic groups. Now, these groups produce additional crosslinks via H-bonding interactions (31) and hence, gel particles become quite compact and remain nearly unswollen. In this condition, the diffusion of drug molecules into gel particles is almost restricted and hence, minimum drug adsorption is observed. Thus, it can be seen that maximum drug sorption is observed at pH 6.0 of the sorption system. We also increased the pH of the sorbate solution beyond 6.0, but there was not any noticeable increase or decrease observed. Hence, all the experiments were carried out at self pH which was found to be nearly 6.2 to 6.6 in all the experiments.

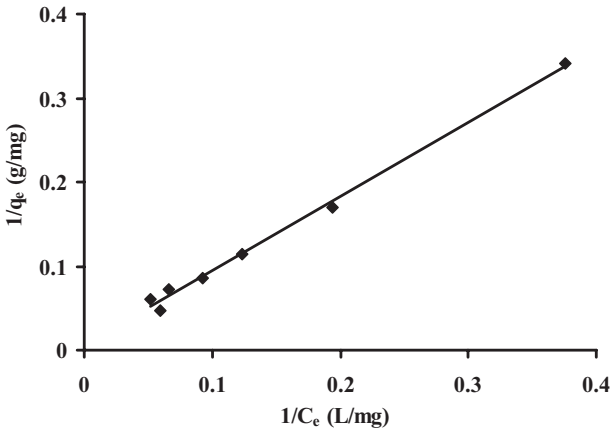

Fig. 6. Langmuir plot for the sorption of Ciprofloxacin onto poly(AAm-co-IA) at 28°C.

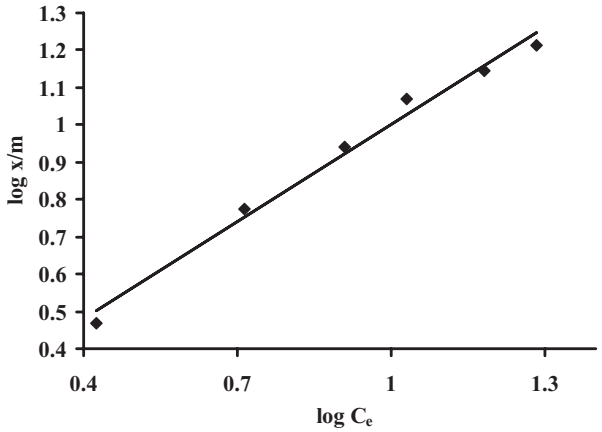

Fig. 7. Freundlich plot for the sorption of Ciprofloxacin onto co-polymeric sorbent at 28°C..

3.4 Equilibrium Sorption Studies

The study of equilibrium sorption is essential to design a plant based on sorptive removal process (32). The sorption equilibrium indicates how the sorbate molecules distribute themselves between the liquid phase (solution) and the solid phase (sorbent) at the equilibrium state (33). In order to describe sorption equilibrium data of CF on copolymeric sorbent, Langmuir, Freundlich and Temkin isotherm models were used which may described as below.

Langmuir model (34) assumes monolayer coverage of sorbate over a homogeneous sorbent surface and is given as:

$$\frac{1}{q_e} = \frac{1}{Q_o} + \frac{1}{Q_o b} \cdot \frac{1}{C_e} \tag{3}$$

Where Q_o(mg g^{-1})is the maximum sorption capacity corresponding to complete monolayer coverage on the sorbent surface and b (L mg^{-1}) is the Langmuir constant related to the heat of sorption.

Freundlich isotherm (35) assumes that the adsorption process takes place on a heterogeneous surface and is given as:

$$\log q_e = \frac{1}{n} \log C_e + \log K_F \tag{4}$$

Where K_F (mg/g $(L/mg)^{1/n}$) is Freundlich constant related to sorption capacity and n refers to sorption intensity.

Finally, Temkin isotherm (36) considers the effects of some indirect sorbent/sorbate interactions on the uptake process and is given as:

$$q_e = \frac{RT}{b_T}.\ln A_T + \frac{RT}{b_T} \ln C_e \tag{5}$$

Where $A_T$and b_T are Temkin constants.

Figures 6–8 show Langmuir, Freundlich and Temkin isotherms respectively, drawn using the equilibrium uptake data obtained with initial concentrations of drug solutions in the range of 10 to 70 mg L^{-1} at 28°C. It was found that all the three isotherm models fitted well on uptake data and, based on their regression values, the order of fitness was Langmuir > Freundlich > Temkin. The various isotherms parameters have been given in Table 2. It is clear that a fair maximum sorption capacity value of 178.5 mg g^{-1} (i.e. Q_o) is obtained at 28°C, which indicates high removal efficiency of the copolymeric ion-exchanger.

Finally, in order to investigate the mode of uptake process i.e., whether physical or chemical sorption, the equilibrium sorption data was also applied to the Dubinin-Radushkevich (D-R) isotherm model, this is given as (37):

$$C_{ad} = C_m.\exp(-B\varepsilon^2) \tag{6}$$

Where $C_{ad}$is the amount of sorbate adsorbed in moles g^{-1}, $C_m$is the maximum amount of drug that could be adsorbed on copolymeric sorbent under the optimized experimental conditions, B is a constant with a dimension of energy, and Polyanyi potential, $\varepsilon = RT \ln(1 + 1/C_e)$, where R is the gas constant in kJ $mol^{-1}K^{-1}$, T is the absolute temperature in K and, $C_e$is the equilibrium concentration (mol L^{-1}) of

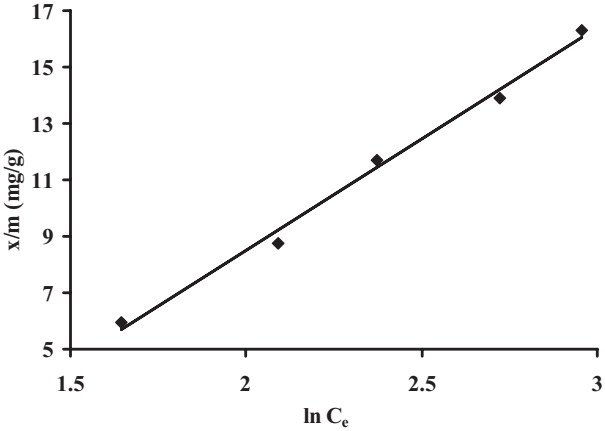

Fig. 8. Temkin plot for drug uptake onto co-polymeric sorbent at 28°C.

Table 2. Parameters for various isotherms obtained using equilibrium sorption data at 28°C

Langmuir Isotherm			*Freundlich Isotherm*			*Temkin Isotherm*		
Q_o *(mg* g^{-1}*)*	*b (L* mg^{-1}*)*	R^2	*n*	K_F *(mg/g)(L/mg)*$^{1/n}$	R^2	a_T	b_T	R^2
178.57	6×10^{-3}	0.9945	1.15	1.351	0.9827	0.3943	315.37	0.9927

drug solution .The linearized form may be written as:

$$\ln C_{ad} = \ln C_m - B\varepsilon^2 \quad (7)$$

When ln C_{ad} was plotted against ε^2, a linear plot was observed (Fig. 9) with a fairly high regression value of 0.9917. The computed value of B from the slope of straight line was found to be 6.4×10^{-3} kJ mol^{-2}. From the calculated value of B, the mean sorption energy was computed as:

$$E = \frac{1}{\sqrt{-2B}} \quad (8)$$

Which is the free energy transfer of one mole of solute from infinity to the surface of sorbent. The numerical value of B, as evaluated using Equation 8, was 8.839 kJ mol^{-1}which lies just within the prescribed range of 8–16 kJ mol^{-1} for ion-exchange. In this way, it may be concluded that sorption of the drug is mainly governed by an ion-exchange process as also predicted in a previous section while discussing pH effect.

3.5 Dynamic Sorption Studies

The effect of contact time on drug sorption was studied for sorbate solutions with initial concentrations of 10, 20 and 30 mg L^{-1} at 28°C.The results, as depicted in the Figure 10, shows that the amount of drug sorbed per unit mass of sorbent increases with the increase in initial concentration. The amounts of drug sorbed at equilibrium were found to be 7.75, 18.21 and 24.17 mg g^{-1} for the sorbate solutions with initial concentrations of 10, 20 and 30 mg L^{-1}, respectively. In fact, the initial concentration provides an important driving force to overcome all mass transfer resistances of the drug between the aqueous and solid phases (38). Hence, a higher initial concentration of CF will enhance the adsorption process. Figure 10 also shows that rapid sorption of drug takes place in the first five minutes and thereafter, the drug uptake becomes quite slow and finally reaches equilibrium.

3.6 Sorption Kinetic Models

The most commonly used kinetic models, namely pseudo first order and pseudo second order, were employed to make quantitative interpretation of the kinetic data displayed in Figure 10.

A simple pseudo first order kinetic model (39) is given as:

$$\log(q_e - q_t) = \log q_e - \frac{k_{ads}}{2.303}t \quad (9)$$

Where q_t(mg g^{-1}) is the amount of drug sorbed on the surface of copolymeric sorbent at time t and k_{ads} (min^{-1}) is the equilibrium rate constant of pseudo first order sorption. Utilizing the uptake data, displayed in Figure10, we plotted graphs between log (q_e–q_t) and t, which were found to be almost linear, as depicted in Figure 11, however, with poor regression. In addition to pseudo first order, use of pseudo second order is also very common. There are four types of linear pseudo second order kinetic models (40), of which

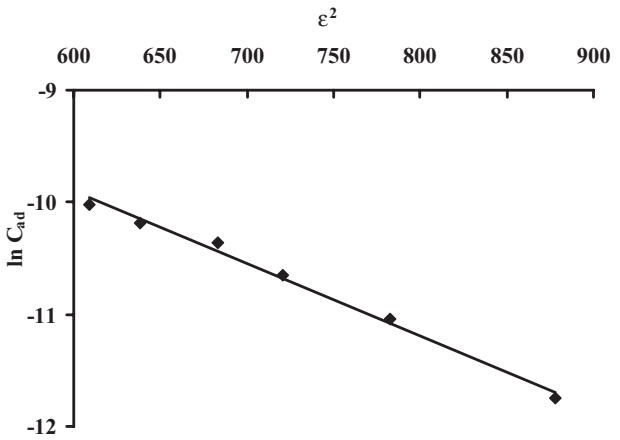

Fig. 9. Dubinin-Radushkevich isotherm for sorption of drug onto sorbent at 28°C.

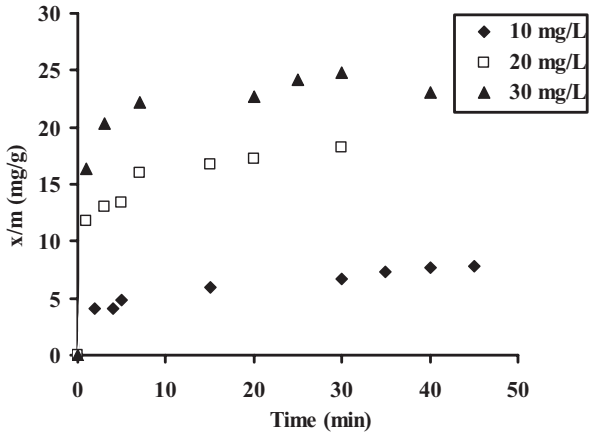

Fig. 10. Kinetics of adsorption of drug onto copolymeric sorbent at 28°C.

Table 3. Parameters for pseudo first and pseudo second order kinetic models obtained using uptake data at 28°C

	Pseudo first order			*Pseudo second order*			
Conc. (mg/L)	R^2	k_{ads} (min^{-1})	q_e (mg/g)	R^2	k_{ads} $(min^{-1}\ mg^{-1}g)$	q_e (mg/g)	q_{exp} (mg/g)
10	0.9601	45.0×10^{-3}	4.764	0.9926	58×10^{-3}	7.99	7.75
20	0.9000	70.9×10^{-3}	6.358	0.9949	52.7×10^{-3}	18.11	18.21
30	0.9614	45.83×10^{-3}	12.891	0.9945	34.0×10^{-3}	24.39	24.17

most popular linear form is:

$$\frac{t}{q_t} = \frac{1}{K_{2ads}} q_e^2 + \frac{1}{q_e} t \qquad (10)$$

Where q_e is the amount of drug sorbed at equilibrium, k_{2ads} is second order rate constant (g/mg min). The kinetic drug uptake data, when applied on the above Equation 10, yielded linear plots between t/q_t and t with fairly higher regression of 0.9926, 0.9949 and 0.9945 with solutions of concentrations 10, 20 and 30 mg L^{-1}, respectively (Fig. 12). Now, using slopes and intercepts of these linear plots, obtained for pseudo first order and second order kinetic models, adsorption rate constants and equilibrium drug uptake were evaluated and are given in the Table 3. It can be seen that regression values, obtained for pseudo second order kinetic plots are much higher than those obtained for first order kinetic plots. In addition, it is also clear from Table 3 that the amounts of drug sorbed at equilibrium (i.e., q_e) evaluated using those pseudo second order kinetic model are very close to the experimental values of q_e. In this way, it may be concluded that pseudo second order kinetic model describes the kinetic uptake data most successfully. Here, it is also worth mentioning that we also applied a simple Elovich model (41) on uptake data but the regression was quite poor.

3.7 Macro and Micro-pore Diffusion

The uptake mechanism of a sorbate onto the sorbent follows three steps viz. film diffusion, pore diffusion and intraparticle transport (42). The slowest of the three steps controls the overall rate of the sorption process. Generally, pore diffusion and intraparticle diffusion are often rate limiting in a batch reactor (26). The adsorption rate parameter which controls the batch process for most of the contact time is the intraparticle diffusion. The possibility of intraparticle diffusion resistance affecting adsorption was explored by using the intraparticle diffusion model, given as (43):

$$q_t = k_{id} t^{1/2} + I \qquad (11)$$

Where k_{id}(mg g^{-1} $min^{-1/2}$) is the intraparticle diffusion rate constant and I is the intercept of plot of q_t vs. $t^{1/2}$. If this linear plot passes through origin. then intraparticle diffusion is the rate controlling step. In case the straight line does not pass through origin, it indicates that there is difference between the rate of mass transfer in the initial and final steps of adsorption, and some other mechanism along with intraparticle diffusion is also involved (44). To investigate this, q_t vs. $t^{1/2}$ plots were obtained for dynamic uptake of drug from solutions with initial concentrations of 10, 20 and 30 mg L^{-1}. The results, as shown in the Figure 13, indicate that plots are non-linear in the initial stage, then possess linearity and do not pass through origin.

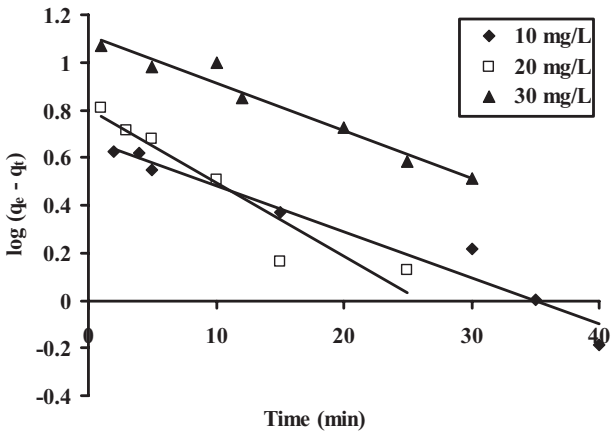

Fig. 11. Pseudo first order kinetic plots for sorption of Ciprofloxacin onto copolymeric sorbent at 28°C.

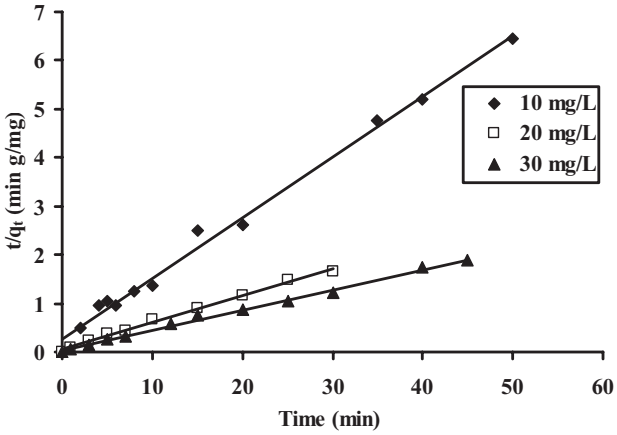

Fig. 12. Pseudo second order kinetic plot for sorption of drug Ciprofloxacin onto copolymeric sorbent at 28°C.

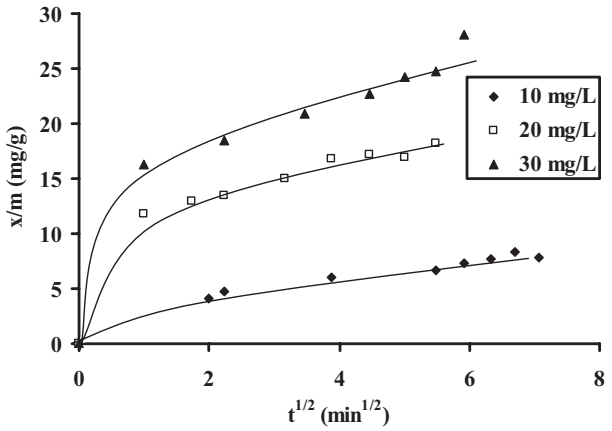

Fig. 13. q_t vs. $t^{1/2}$plots for calculation of rate constant for intraparticle diffusion.

The values of intraparticle diffusion rate constants k_{id}, as determined using slopes of the linear plot of later portions of curves were found to be 99.7×10^{-2}, 143.0×10^{-2} and 216.4×10^{-2} mg g^{-1} $min^{-1/2}$, respectively. In addition, the intercepts of linear plots are 1.9, 6.1 and 13.6, respectively which represent boundary layer thickness. Therefore, it may be concluded that with an increase in initial concentrations of sorbate solutions, the corresponding values of k_{id} and boundary layer thickness increase.

3.8 Regeneration Study

The industrial applications of sorbent depend upon its cost-effectiveness, which in turn depends upon its reusability. In order to investigate the regenerating tendency of present copolymeric sorbent, the sorbent was put in 50 ml drug solution to attain equilibrium sorption and the drug loaded sorbent was now placed in a KCl solution of 1M concentration, for desorption. It was found that nearly 83% amount of drug was desorbed which could be attributed to the fact that ionized drug molecules present within the sorbent induced ion-exchange process with external K^+ions, thus resulting in a higher degree of desorption. However, when the regenerated sorbent was again put in drug solution for sorption study, it was found that the amount of drug adsorbed per gm of sorbent was nearly 30% of the initial sorption. This indicated that although the sorbent was regenerated, it could not be very effective in readsorption of the drug. A possible explanation for poor uptake efficiency of regenerated sorbent may be that the K^+ions present at sorption sites within the sorbent may have poor exchangeability with external drug molecules. This resulted in poor drug uptake.

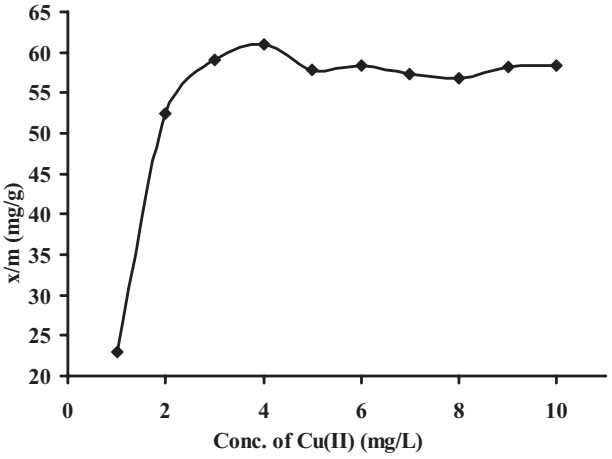

Fig. 14. Effect of presence of Cu(II) ions on drug uptake.

3.9 Effect of Cu-ions on Drug Uptake

The presence of other toxic metal ions, if present in the drug solution, is expected to influence the drug uptake. To investigate this, the drug uptake was studied in the presence of Cu(II) ions with their concentrations in the range of 1.0 to 10.0 mg L^{-1}at 28°C. The results obtained were just opposite to expectations and have been well depicted in the Figure 14. It is clear that the presence of Cu(II) ions enhances the drug uptake, which later attains almost saturation value of 60 mg/g. The observed findings may be explained as below.

When Cu(II) ions are present in the sorption system, they compete with drug molecules and are preferably coordinated with $-NH_2$ groups of poly acrylamide chains. In this way, Cu(II) binds with two $-NH_2$ groups belonging to two opposite polymeric chains as shown in Figure 15. As two residual valencies of Cu(II) are still unoccupied, they might be occupied by drug molecules. In addition, drug

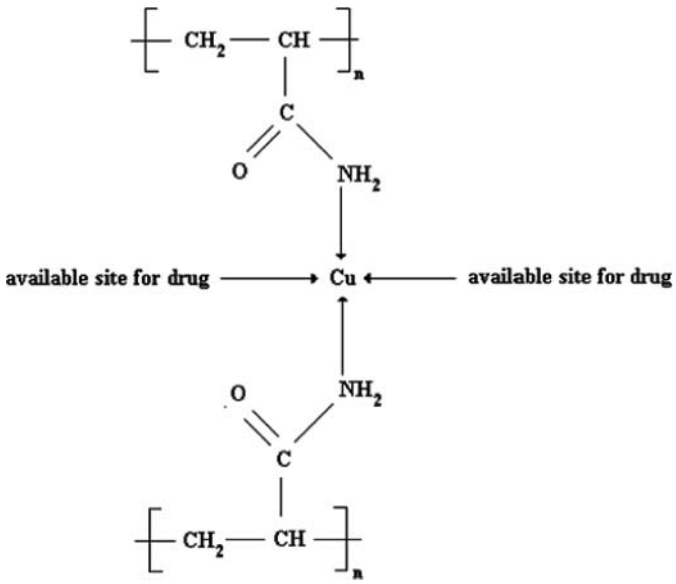

Fig. 15. Scheme showing availability of binding sites for drug ions onto coordinated copper.

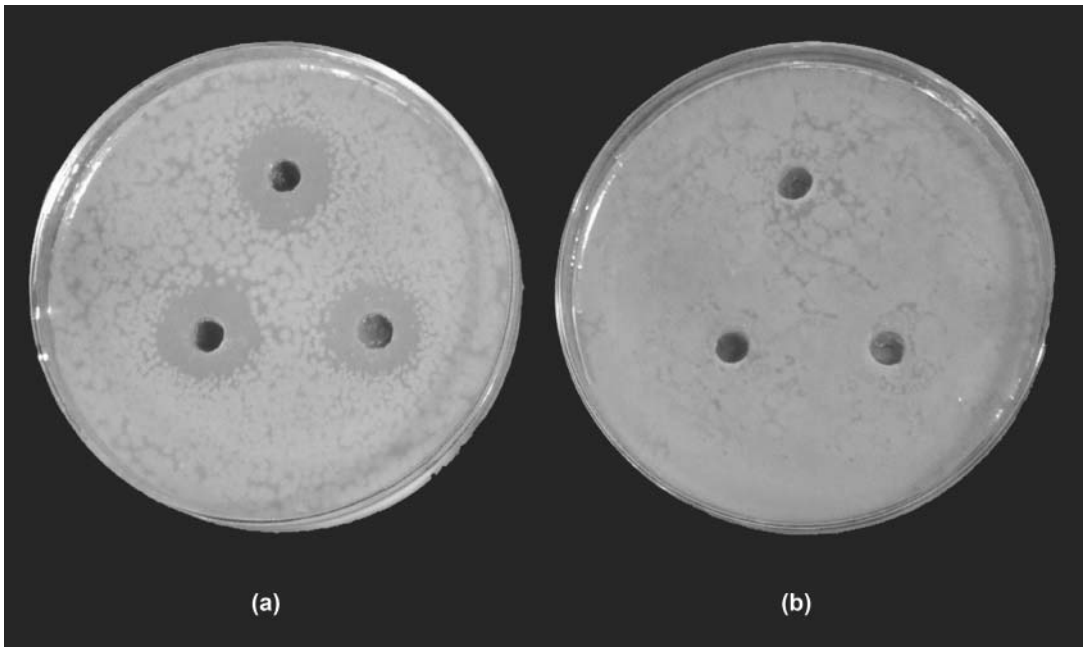

Fig. 16. Antibacterial Study: zone of inhibition in the petridishes supplemented with (a) original drug solution and (b) drug solution left after adsorption.

is also adsorbed. Hence ion-exchange between counter H^+ ions of itaconic acid moieties of copolymer chains and drug positive ions present in the external solution, and overall affects the presence of Cu(II) ions which results in higher drug uptake.

3.10 Antibacterial Study

The major disadvantage of presence of drugs in aquatic system is that they kill micro-organisms like bacteria, fungi which take up toxic metal ions and thus help to protect the aquatic environment. So, the presence of drugs increases the metal ion toxicity by reducing the micro-organisms. Figure 16(a) shows the growth of bacteria in Petri dishes, supplemented with a drug solution of concentration 3.0 mg L^{-1} and Figure 16(b) that contains drug solution left after adsorption. It is clear that the Petri dish containing the original drug solution shows greater inhibitory action of drug. Whereas, there is a larger population of colonies in the Petri dish containing drug solution which remained after adsorption.

4 Conclusions

From the above study, it may be concluded that poly(AAm-co-IA) is a potential sorbent for the removal of Ciprofloxacin from aqueous solution. The sorption process is best described by the Langmuir isotherm model and the ion-exchange appears to be the key factor to govern the uptake process. Although the proposed sorbent appears to exhibit fair removal efficiency from aqueous drug solution, but its potential needs to be tested with municipal wastewater which has a very complex composition, depending upon waste origin and treatment efficiency (45). For example, Bodkhe (46) has reported that municipal water in some cities in India, contains total sulfide (2 to 6 ml^{-1}), oil and grease (15 to 20 mg ml^{-1}), phenols (30 to 40 mg ml^{-1}), alkalinity as $CaCO_3$ (230 to 300 mg ml^{-1}), and phosphorus (25 to 50 mg ml^{-1}). Therefore, it is required to test removal efficiency of polymeric sorbent with municipal water as well. The co-polymeric sorbent can be regenerated, although it has poor reusability.

Acknowledgements

The authors are thankful to Dr. O. P. Sharma for his unconditional support and for providing necessary facilities.

References

1. Aksu, Z., and Tunc, O. (2005) *Process Biochem.*, 40(2), 831–847.
2. Seino, A., Hasegawa, Y., and Masunaga, S. (2004) *J. Japan Society on Water Environ.*, 27(10), 693–698.
3. Ternes, T.A. (1998) *Water Res.,* 32(10), 3245–3260.
4. Wang, Q.L., Ding, De-Xin., Hu, E., Yu, R., and Qlu, G. (2008) *Transactions of Nonferrous Metals Society of Chin*a, 18(5), 1529–1532.
5. Segura, P.A., Francois, M., Gagnon, C., and Sauve, S. (2009) *Environ. Health Perspect.*, 117(4), 675–684.
6. Cabello, F.C. (2006) *Environ. Microbial.*, (7), 1137–1144.

7. Cordova-Kreylos, A.I., and Scow, K.M. (2007) *ISMEJ*, (1), 585–595.
8. Ghosh, S., and Lapara, T.M. (2007) *ISMEJ*, (1), 191–203.
9. Kummerer, K. (2009) *Chemosphere*, 75, 417–434.
10. Koyuncu, I., Arikan, O.A., Wiesner, M.R., and Rice, C. (2008) *J. Membrane Sci*., 309(1–2), 94–101.
11. Choi, K., Kim, S., and Kim, S-H. (2008) *J. Hazard. Mater.,* 151(1), 38–43.
12. Radjenovic, J., Petrovic, M., and Barcelo, D. (2007) *Anal. Bioanal. Chem*., 387(3), 1365–1377.
13. Gauch, A., Tuqan, A., and Assi, H.A. (2009) *Environ. Pollut.,* 157(4), 1626–1635.
14. Dutta, M., Baruah, R., and Dutta, N.N. (1997) *Sep. Purification Technol*., 12(2), 99–108.
15. Budyanto, S., Soedjono, S., Irawaty, W., and Indraswati, N. (2008) *J. Environmental Protection Sci*., 2, 72–80.
16. Adriano, W.S., Veredas, V., Santana, C.C., and Goncalves, L.R.B. (2005) *Biochem. Eng. J*., 27 (2), 132–137.
17. Pisarev, O.A., Ezhova, N.M., and Garkushina, I.S. (2009) *Russian J. Physical Chem*., 83(1), 17–27.
18. Valtchev, M., Palm, B.S., Schiller, M., and Steinfeld, U. (2009) *J. Hazard. Mater*., 170, 722–728.
19. Bajpai, S.K., and Bhowmik, M. (2010) *J. Appl. Poly. Sci*., 117(5), 3615–3622.
20. Khoder, M., Tsapis, N., Hugust, H., Besnard, N., Gueutin, C., and Fattal, E. (2009) *Int.* J. Pharmaceutics, 379, 251–259.
21. Owens, R.C., and Ambrose, P.G. (2005) *Clin. Infect. Dis*., 41 Suppl.(2), 144–157.
22. Drlica, K., and Zhao, X. (1997) *Mol. Biol. Rev*., 61(2), 377–392.
23. Bajpai, S.K., and Johnson, S. (2005) *React. Funct. Polym.,* 62(2), 271–283.
24. Bajpai, S.K., and Tankiwale, R. (2008) Polym. Int., 57(1), 57–65
25. -S-Z. E., El-Ashtoukhy, Amin, N.K., and Abdelwahab, O. (2008) *Desalination*, 223(1–3), 162–173.
26. Vimala, V., Sivudu, K.S., Mohan, Y.M., Sreedhar, B., and Raju, K.M. (2009) *Carbohyr. Polym*., 75, 463–471.
27. Bajpai, A.K., and Bajpai, S.K. (1995) *Coll. and Interf*., 273(10), 1028–1032.
28. Anirudhan, T.S., Suchithra, P.S., and Radhakrishnan, P.G. (2009) *Appl. Clay Sci*., 43, 1336–1342.
29. Pisal, S., Zainmuddin, R., Nalawade, P., Mahadik, K., and Kadam, S. (2004) *AAPS Pharma. Sci. Tech*., 5(3).
30. Sen, M., Yakar, A., and Guven, O. (1999) *Polymer*, 40, 2969–2974.
31. Bajpai, S.K. (2001) *J. Appl. Polym. Sci*., 80(14), 2782–2789.
32. Chandra, T.C., Mirna, M.M., Surdayanto, Y., and Ismadji, S. (2006) *Chem. Eng. J*., 127, 121–129.
33. Hameed, B.H., Din, A.T.M., and Ahmad, A.L. (2007) *J. Hazard. Mater.,* 141(2), 819–825.
34. Langmuir, I. (1918) *J. Am. Chem. Soc*., 40(8), 1361–1403.
35. Freundlich, H. (1906) *Z. Phys. Chem*., 57, 384–470.
36. Temkin, M.J., and Pyzhev, V. (1940) *Acta Physiochem*., 12, 217–222.
37. Ahmad, S., Khalid, N., and Daud, M. (2002) *Sep. Sci. Technol*., 37(2), 343–362.
38. Hameed, B.H. (2009) *J. Hazard. Mater.,* 161(2–3), 753–759.
39. Lagergren, S., and Vetenskapsakademiens, K.S. (1898) *Handlingar*, 24(3), 1–39.
40. Ho, Y.S., and McKay, G. (1998) *Chem. Eng. J*., 70(2), 115–124.
41. Badmus, M.A.O., Audu, T.O.K., and Anyata, B.U. (2007) *Turkish J. Eng. Env. Sci.,* 31, 251–263.
42. Vishwanathan, N., and Meenakshi, S. (2008) *J. Fluorine Chem*., 129(5), 503–509.
43. Cheung, W.H., Szeto, Y.S., and McKay, G. (2007) *Bioresource Technol*., 98(15), 2897–2904.
44. Baral, S.S., Das, S.N., and Rath, P. (2006) *Biochem. Eng. J.,* 31(2), 216–2904.
45. Chang, A.C., Page, A.L., and Bingham, F.T. (1981) JSTOR*: J (Water Pollution Control Federation)*, 53(2), 237–245.
46. Bodkhe, S.Y. (2009) *J. Environmental Management*, 90, 2488–2493.