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Research Article

Pharmaceutical analysis for Novel drug formulation

Investigation of Adsorptive Properties of Surfactant Modified Sepiolite for Removal of Ciprofloxacin

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Abstract: Pharmaceutical residues, which are considered as emerging contaminants, have been frequently detected in various water including treated water, surface water, and underground water. Furthermore, it may pose a serious risk to the living organisms by enhancing bacterial drug resistance. However, the removal of CIP from aqueous solution is difficult by present water treatment methods. The previous study indicated that the removal of CIP by conventional wastewater treatment technologies is generally incomplete. The aim of this study was to evaluate the efficiency of surfactant (cetyltri-methyl-ammonium bromide)-modified Sepiolite (SMS) for Ciprofloxacin antibiotics (CIP) adsorption in a batch mode technique. The effects of different system variables, adsorbent dosage, initial CIP concentration, temperature contact time were investigated and optimal experimental conditions were ascertained. The results showed that as the amount of the adsorbent is increased, the percentage of CIP removal increase accordingly. Optimum temperature value for CIP adsorption was 50 °C. Maximum CIP was sequestered within 60 min from the start of every experiment. The results also showed that the best test conditions were obtained at i) initial concentration of CIP 10 mg/L and adsorbent dosage 2 g/L as working solution have been selected as the optimum conditions by the batch process; ii) the removal percentage and the maximum adsorption capacity were found to be 99.1% and 63.84 mg/g iii) Four well-known kinetic models, the pseudo-first- and pseudo-second-order, Elovich and Intra-particle diffusion were used to correlate the adsorption kinetic data, with the pseudo-second-order model giving better results; iv) Negative value of ΔG° and positive value of ΔH° indicates the feasibility of the process and indicates the spontaneous and endothermic nature of the adsorption; v) SMS adsorbent can be an attractive option for CIP antibiotic removal from diluted industrial effluents since test reaction made on simulated antibiotic wastewater showed better removal percentage of CIP.

Keywords: Adsorption; Surfactant Modified Sepiolite; Ciprofloxacin; Kinetics, Thermodynamic

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1. INTRODUCTION

Pharmaceuticals are an example for the variety of man-made trace pollutants that are introduced in surface or subsurface water bodies [1, 2.] Pharmaceuticals have been identified in the environment, including antibiotics, analgesics, psychiatric drugs, and natural and synthetic hormones [3]. Unused human pharmaceuticals may also enter the environment through landfill leachate [4]. The fluoroquinolone antibiotic is one of the pervasive pharmaceutical groups, which cannot be biodegraded at low and notable concentrations [5, 6]. As one species of fluoroquinolone, ciprofloxacin (CIP) is frequently used and detected in the environment due to its broad-spectrum antibacterial property and high mobility [7]. Furthermore, it may pose a serious risk to the living organisms by enhancing bacterial drug resistance [8]. Due to the chemical structure of antibiotics, they act as resistant to many chemicals oxidizing agents and heat and are biologically non-degradable [9, 10]. So it is difficult to decolorize the effluents, once released into the aquatic environment [11, 12]. Many of the methods are available for the removable pollutants from water, the most important of which are reverse osmosis, ion exchange, precipitation and adsorption [13]. Adsorption process has been found to be superior technique for treating antibiotics effluents due to simplicity and insensitivity to toxic substance [14, 15]. Although the activated carbon is most effective for absorption of antibiotics, it has some disadvantages such as (i) high adsorbent cost, (ii) problems of regeneration and difficulties of separation of powdered activated carbon from waste water for regeneration. These are expensive and hence there is an increasing need for equally effective but commercially low cost sorbents [16, 17]. Therefore, researchers are continually in search for cheaper, easily obtainable materials for the adsorption of antibiotics [18, 19]. Natural clays for antibiotics removal from wastewater such as zeolite, bentonite, kaolinite and sepiolite are investigated as low-cost and readily available adsorbents [20, 21]. Sepiolite is a natural hydrated magnesium silicate with a wide range of industrial applications derived mainly from its adsorptive properties [22-24]. It has a fibrous structure formed by an alteration of blocks and channels that grow up in the fiber direction [25]. Each block is constructed of two tetrahedral silica sheets enclosing a central magnesia sheet [26]. The present article reports the feasibility of utilizing SMS as a low cost adsorbent material for the removal of CIP ions from wastewater. In the batch mode studies, the dynamic behaviour of the adsorption was investigated on the effect initial CIP concentration, temperature, SMS dosage and contact time. The thermodynamics and kinetics adsorption were also studied.

2. MATERIALS AND METHODS

2.1 Reagents and solutions

All reagents used were of analytical grade chemicals and were obtained from Merck (Merck AG., Darmstadt, Germany). Ciprofloxacin (molecular weight 331.34 g/mol, CAS Number 85721-33-1 and Molecular Formula $C_{17}H_{18}FN_3O_3$) used as adsorbate, obtained from Sigma Aldrich Co, and shown in Fig 1. A stock solution of 1000 mg/L was prepared by dissolving appropriate amount of CIP in1000 ml double distilled water in a volumetric flask, different concentrations were prepared by diluting the stock solution to the initial concentrations ranging from 10-100 mg/L.

2.2 Synthesis of Surfactant-Modified Sepiolite (SMS)

The surfactant-modified sepiolite was synthesized by the following steps. For synthesis, 50 g sepiolite was put in 500 mL of water containing 10 g of CTAB. The reaction components were stirred at 25 °C for 12 h. The product was filtered and washed repeatedly with distilled water [27]. The surfactant-modified sepiolite was dried at 110 °C for 6 h and stored in a desiccator.

2.3 Batch experiments

In order to investigate the behavior of the SMS, adsorption experiments were carried out. The amount of adsorbed CIP per gram of SMS (mg/g) at time t (min) was calculated using the following equation [28]:

$$\boxed{q_t = (C_0 - Ct) \times V/M}$$

Where q_t (mg/g) is the amount of adsorbed CIP per gram of SMS at time t (min), C_0 is the initial concentration of CIP solution (mg/L), Ct is the concentration of CIP solution (mg/L) at time t (min), V is the volume of the solution (L) and M is the mass of the adsorbent (g). The initial concentrations of CIP solutions were in the range of 10 to 50 mg/L and experiments were performed at 20 °C. The initial CIP concentration, contact time, SMS dose and temperature were selected as experimental parameters. The pH of the solution was adjusted with NaOH or HNO_3 solution by using a pH-meter. After the adsorption equilibrium is reached, the suspensions were centrifuged at 3600 rpm and the concentration of CIP remaining in the supernatant determined using UV-vis spectrophotometer at λ_{max}= 274 nm. The uptake of CIP ions was calculated by the difference in their initial and final concentrations. All experiments were repeated at least twice. The adsorption capacity of CIP was calculated through the following equation [29]:

$$\boxed{q_e = (C_0 - Ce) \times V/M}$$

Where q_e is the amount of adsorption CIP (mg/g) at equilibrium, C_0 is the initial concentration of CIP in solution (mg/L), C_e is the equilibrium concentration of CIP in solution (mg/L), m is the mass of adsorbent used (g) and V is the volume of CIP solution (L).

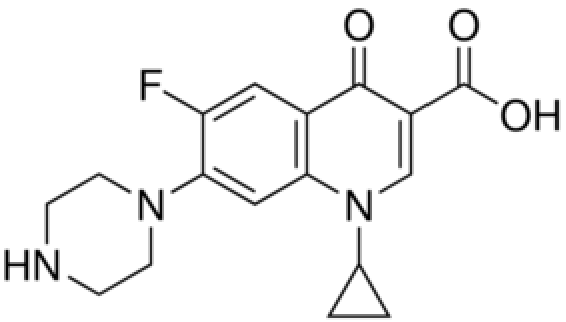

Fig 1. Chemical structure of CIP

3. RESULTS AND DISCUSSION

3.1 Effect of contact time

From Figs 2 and 3, it can be observed that the percent removal efficiency and adsorption capacity of CIP onto SMS increased with increase of contact time and reached equilibrium in 60 min. Increase in contact time after 60 min cannot enhance the adsorption of CIP onto SMS. In the beginning, the percent of CIP was rapidly increased with the increase of adsorption time at first 30 min. Due to the adsorption more molecules of CIP on the unsaturated surface area of SMS [30]. The initial rate of adsorption capacity was rapid in the first stage due to the larger surface area and the availability of the binding active sites of the adsorbent at the first minutes and the driving force provided by the initial concentration at the first stage which overcomes all mass transfer resistance of CIP between the aqueous and solid phases [31, 32].

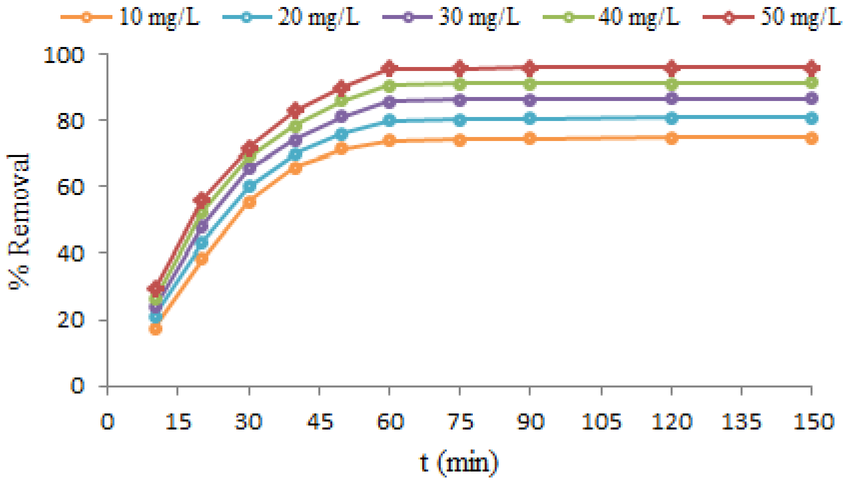

Fig 2. Effect of contact time on the adsorption of CIP onto SMS (adsorbent dose = 2 g/L, pH = 7, tem=20 ± 2 ◦C)

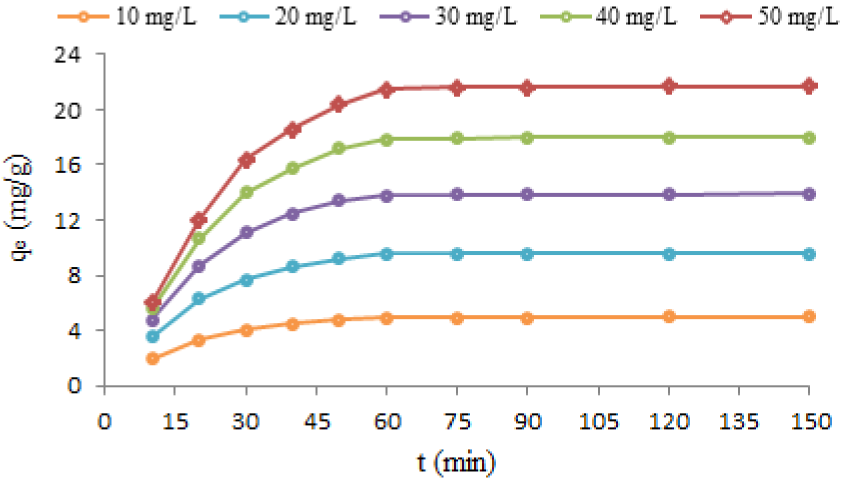

Fig 3. Effect of contact time on the adsorption capacity (adsorbent dose = 2 g/L, pH = 7, tem=20 ± 2 ◦C)

3.2 *Effect of adsorbent dosage*

The effect of SMS mass on the adsorption CIP is shown in Fig 4. The trend revealed a progressive increase in the amount of CIP adsorbed as adsorbent dosage increased from 0.25 to 2 g. The percentage of CIP removed increased from 31.92 to 86.17%, and then the value of percentage removal were very close indicating that adsorption was almost finished with 2 g of the SMS and the equilibrium take place. It is reasonable that increasing the adsorbent dose increased the surface area, thus providing an increase in the available active sites for the adsorption [33]. Similar trend was also observed by [34, 35], while adsorption capacity decreased with increasing amount of SMS. For instance a decrease from 63.84 to 14.36 mg/g was recorded when the adsorbent mass increased from 0.25 g to 3 g/L. This trend can be explained as a result of overlapping or aggregation of adsorption sites resulting in a decrease in the total adsorption surface area available to the CIP and an increase in the diffusion path length[36, 37].

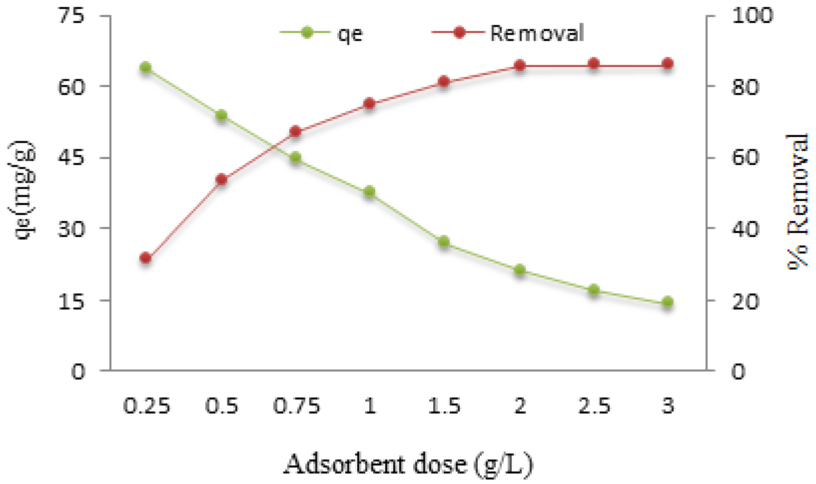

Fig 4. Effect of adsorbent dosage on efficiency of CIP adsorption
(C_0: 50 mg/L, tem: 20 ± 2 °C, pH: 7, time: 60 min)

3.3 *Adsorption kinetics*

The study of adsorption kinetics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid – solution interface. The kinetics of CIP adsorption on the SMS was analyzed using Pseudo first order, Pseudo second order, and Elovich and Intra-particle diffusion kinetics models. The conformity between experimental data and the kinetics models was expressed by the correlation coefficients (R^2) value, the R^2 values close or equal to 1. A relatively high R^2 value indicates that the model successfully describes the kinetics of CIP adsorption. The first-order rate expression of Lagergren equation is given as [38, 39]

$$\boxed{\text{Log}\,(q_e - q_t) = \log q_e - \frac{K_1}{2.303}t}$$

Where q_e and q_t are the amounts of CIP adsorbed on adsorbent at equilibrium and at time t, respectively (mg/g) and K_1 is the rate constant of first order adsorption (1/min). The slope and intercept of plot of log (q_e-q_t) vs. t were used to determine K_1 and q_e. These values are given in Table 1. From the table the q_e values calculated from the Pseudo first order model is less than that of the experimental value. It is does not fit for pseudo first order kinetics. The second-order kinetic rate equation is given as [40]:

$$\boxed{\frac{t}{q_t} = \frac{1}{k_2\, qe^2} + \frac{t}{qe}}$$

Where K_2 is the rate constant of Pseudo-second order adsorption (g/mg.min) and amounts of CIP adsorbed on adsorbent at equilibrium (mg/g). The plot of t/q_t vs. t should give a linear relationship from which K_2 and q_e can be determined from the slope and intercept of the plot, respectively. The plot and parameter of Pseudo second order of CIP on SMS are presented in Fig. 5 and Table 1. From the table q_e values calculated from the Pseudo second order model are nearly equal to the experimental value and correlation coefficient (R^2) value are high compared with Pseudo first order model. So that the adsorption of CIP on SMS is to follow the Pseudo second order kinetic model. The Elovich kinetic rate equation is presented as follows[41, 42]:

$$\boxed{q_t = 1/\beta\ \text{Ln}\,(\alpha\beta) + 1/\beta\ \text{Ln}\,(t)}$$

Where α is the initial adsorption rate (mg/g.min), β is adsorption constant (g/mg) during any one experiment. The Elovich model parameters α, β and correlation coefficient R^2 are summarized in Table 1. The correlation coefficient (R^2) is less than that of Pseudo second order model. The intra-particle diffusion model is used here refers to the theory proposed by Weber and Morris based on the following equation for the rate constant [43]

$$\boxed{q_t = K_d\, t^{0.5} + C}$$

Where K_d is the intra particle diffusion rate constant (mg/g.min$^{-1/2}$) and C is constant. If that rate limiting step is intra particle diffusion, the graphical representation of adsorbed CIP q_t versus $t^{0.5}$ yield straight lines passing through the origin and the slope gives the intra particle diffusion rate constant K_d and correlation coefficient (R^2) is indicated in Fig 6. The intra-particle parameters K_d, C and R^2 are summarized in Table 1. From these data inter set value indicate that the line are not passing through origin, therefore some other process that may affect the adsorption.

Table 1: Results of kinetic studies related to the CIP adsorption onto SMS

C_0 (mg/L)	$q_{e\ exp}$ (mg/g)	Intraparticle diffusion			Pseudo-first order		
		K_d	C	R^2	$q_{e\ cal}$	K_1	R^2
10	4.951	0.285	2.167	0.661	2.192	0.076	0.841
20	9.588	0.572	3.981	0.665	4.476	0.068	0.859
30	13.90	0.871	5.392	0.666	7.259	0.033	0.827
40	18.01	1.209	6.154	0.682	11.73	0.018	0.833
50	21.72	1.588	6.372	0.701	14.95	0.011	0.846
C_0 (mg/L)	$q_{e\ exp}$ (mg/g)	Pseudo-second order			Elovich		
		$q_{e\ cal}$	K_2	R^2	α	β	R^2
10	4.951	4.721	0.0081	0.996	2.173	0.417	0.895
20	9.588	9.247	0.0072	0.997	2.064	0.495	0.912
30	13.90	14.08	0.0054	0.995	1.625	0.543	0.876
40	18.01	17.84	0.0033	0.996	1.272	0.568	0.924
50	21.72	20.96	0.0019	0.998	1.124	0.596	0.906

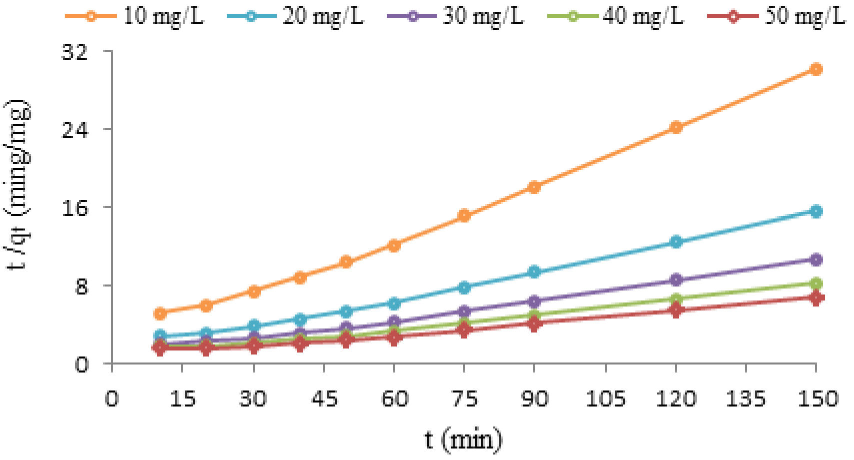

Fig 5. Pseudo-second-order kinetic plot for the removal of CIP by SMS

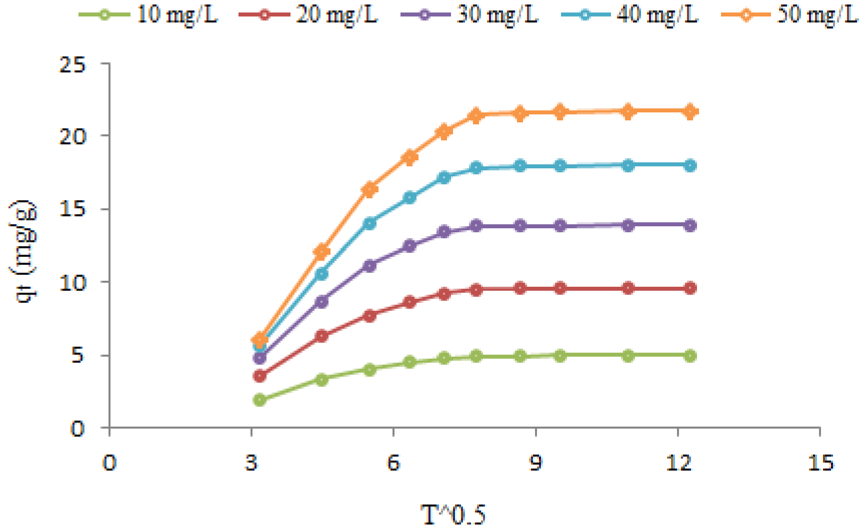

Fig 6. Intra particle diffusion kinetic plot for the removal of CIP by SMS

3.4 Effect of temperature

The effect of temperature of adsorption of CIP is presented in Fig 7. For concentration 50 mg/L CIP was carried out at 10, 20, 30, 40 and 50 °C. The percent removal of CIP increased from 61.52 to 95.76. This indicates that increase in adsorption with increase in temperature may be due to increase in the mobility of the large CIP ions (43, 44). Moreover, increasing temperature may produce a swelling effect within the internal structure of the adsorbent, penetrating the large CIP molecule further [45].

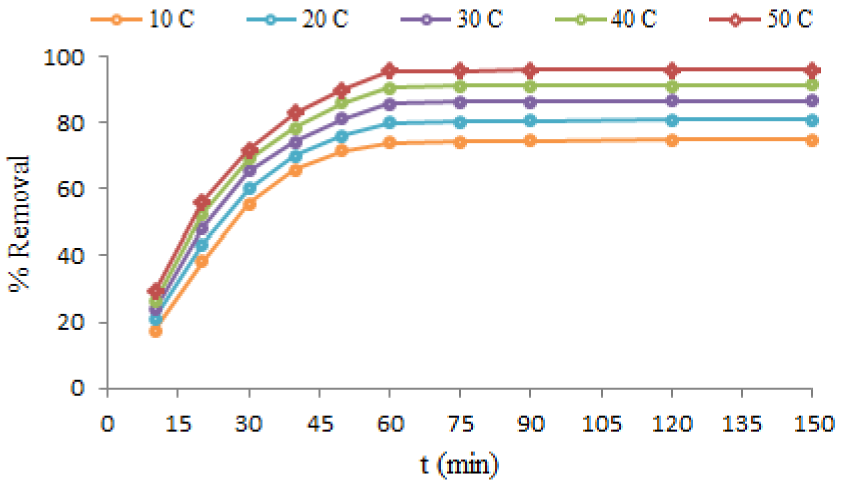

Fig 7: Effect of temperature on efficiency of CIP adsorption (C_0: 50 mg/L, dose: 2 g/L, pH: 7, time: 60 min)

3.5 Thermodynamic parameter

Thermodynamic parameters like ΔH° and ΔS° were evaluated using Van't Hoff's equation (46)

$$\boxed{\ln K_d = (\Delta S_0/R) - (\Delta H_0/RT)}$$

Where K_d is the adsorption equilibrium constant, ΔH° and ΔS°, are the standard enthalpy and entropy changes of adsorption respectively and their values are calculated from the slopes and intercepts respectively of the linear plot of Ln K_d vs. 1/T. The free energy change for the adsorption process ΔG° (kJ/mol) is derived in following equation[47] The values of these parameters were calculated using the following equation and are shown in Table 2

$$\boxed{\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ}$$

The adsorption data indicates that ΔG° were negative at all temperatures. The negative ΔG° confirms the spontaneous nature of adsorption of CIP with SMS. The magnitude of ΔG° suggests that adsorption is physical adsorption process [39]. The positive value of ΔH° were further confirms the endothermic nature of adsorption process. The positive ΔS° showed increased randomness at the solid-solution interface during the adsorption of CIP on SMS. This was also further supported by the positive values of ΔS°, which suggest that the freedom of CIP is not too restricted in the adsorbent, confirming a physical adsorption. The ΔG° value increases with increase in temperature is the increase in enhancement of the adsorption capacity of adsorbent may be due to increase or enlargement of pore size and/or activation of the adsorbent surface [41].

Table 2: Values of thermodynamic parameters for the adsorption of CIP onto SMS

Temperature (K)	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/mol K)
283	-4.514	1.329	17.38
293	-6.172		
303	-7.451		
313	-9.736		
323	-10.895		

4. CONCLUSION

This study shows that SMS can be used effectively for the removal of CIP antibiotics from aqueous solution. 2 g/L is the optimum dosage of SMS to adsorb CIP. The adsorption capacity of the CIP on SMS increased with the increasing of initial concentration of CIP. The equilibrium adsorption capacity increased with temperature. The optimum contact time and temperature were 60 min and 50 °C respectively. The adsorption kinetics was fitted by a pseudo-second order kinetic model. Adsorption of CIP was found to be spontaneous at temperatures under investigation. Thermodynamic parameters suggested that the adsorption of CIP ions on SMS adsorbent was feasible, spontaneous and endothermic in nature. These results show that SMS which have a very low economical value may be used effectively for removal of CIP antibiotic from aqueous solution for environmental protection purpose.

5. ACKNOWLEDGEMENTS

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6. AUTHORS CONTRIBUTION STATEMENT

Dr D. Balarak conceived the idea and also reviewed the manuscript. MS M. Zafariyan and Dr. S. Siddiqui carried out the research study, evaluated the results and drafted the manuscript.

7. CONFLICT OF INTEREST

Conflict of interest declared none.

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