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Decontamination of ofloxacin: optimization of removal process onto sawdust using response surface methodology

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ABSTRACT

Ofloxacin is one of the most used fluoroquinolones, a potent broad spectrum antibiotic class; it is also included in pharmaceutically active compounds that are considered as environmental pollutants. To clean the water systems sorption has been found as an effective way to remove these pollutants. Present study demonstrates the effect of different sawdust treatments on removal of ofloxacin from aqueous solutions. The sorption of ofloxacin by treated sawdust has been optimized by response surface methodology using central composite design. Set of 18 experiments was used and factors as pH, amount of sorbent, contact time, and concentration of sorbate were considered the critical factors to be studied for removal. HCl-treated sawdust was found to have maximum removal efficiency (96%) with the sorption capacity of 47 μmol g^{-1} as compared to other treated sorbents. Amount of sorbent have significantly positive impact on the removal for all three treated sorbents whereas concentration of sorbate has non-significant positive effect for HCl-treated sawdust. Further, sorption isotherms, kinetics, and thermodynamics studies onto HCl-treated sawdust showed that reaction is exothermic and spontaneous in nature and psuedo-second-order is predominant route. Complex sorption mechanism with simultaneous intraparticle diffusion as well as surface adsorption phenomena is responsible for sorption of ofloxacin onto sawdust.

Keywords: Ofloxacin removal; Natural sorbent; Sawdust; Batch sorption; Biomass

1. Introduction

A wide range of substances is reported in the literature as emerging pollutants. In recent years, it has been recognized that antibiotics constitute a new class of water contaminants of emerging concern with adverse effects on the aquatic life [1,2]. Fluoroquinolone (FQ) antibacterial compounds are frequently detected in the aquatic environment [3], FQ have been found in hospital wastewaters (at concentrations ranging from approximately 60–120,000 ng/L), in wastewater treatment plant effluents (~2–580 ng/L), and in surface waters (~5–1,300 ng/L) all over the world [3].

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Ofloxacin, second-generation FQ derivative, is one of the most commonly used drugs to treat expanded gram-negative activity and a typical pathogen coverage, but limited gram-positive activity. These agents are most active against aerobic gram-negative bacilli [4]. Ofloxacin is metabolized to a very small extent compared to other quinolones. In man, approximately 4–5% of the drug is recovered as either desmethyl ofloxacin, which is still active against bacteria, or ofloxacin N-oxide which is inactive. Ofloxacin has a pyridobenzoxazine ring that appears to decrease the extent of parent compound metabolism. Between 65% and 80% of an administered oral dose of ofloxacin is excreted unchanged via the kidneys within 48 h of dosing [5] which also contributes to presence of these in wastewaters beside other sources. Screening of hospital wastewater from Hyderabad City's vicinity (Pakistan) for pharmaceuticals compounds shows the contamination of ofloxacin in the range of 30–70 μg/L (unpublished data from author).

Adsorption is one of the most widely applied techniques for pollutant removal from contaminated medium. The common sorbents include activated carbon, molecular sieves, polymeric adsorbents, and some other low-cost materials [6–9]. Very few studies are carried out for decontamination of ofloxacin from aqueous solutions using sorptive or oxidative technologies [10–13]. Organic waste materials/biomasses have been found efficient for decontamination of toxins [14]. Adsorptive removal of ofloxacin using organic materials like pomegranate peel, black tea leaves, and cork are reported [2,14]. All the three sorbents reported so far showed affinity toward sorption of ofloxacin; however, systematic optimization for optimal efficiency is not worked out. Keeping in view the susceptibility of ofloxacin in aqueous samples and possibility of biomass as effective sorbents; Sawdust (SD) was used as sorbent and optimized with central composite design (COD) for efficient removal. Also, the sorption kinetics, surface interactions are studied using various sorption models.

2. Materials and methods

2.1. Reagents and materials

HPLC grade methanol and formic acid were purchased from Fischer Scientific (UK). OFL (MP Biomedicals, France) pure standard and all other reagents were purchased from Sigma (Germany). SD was collected from a local sawmill. Ofloxacin standard 1,000 μg mL^{-1} was prepared in 5% aqueous methanol and diluted in Millipore water (18 Ω) as working standard.

2.2. HPLC analysis and conditions

A Hitachi 6010 liquid chromatography fitted with a Hitachi L-4200 variable wavelength UV–vis detector, a Rheodyne 7125 injector, and a Hibar® C-18, 250 × 4.6 mm i.d. column (Merck, Germany) were used throughout the study. The CSW32 software (Data Apex) was used for data acquisition and integration. OFL determination was carried out with a mobile phase composition of methanol and 0.1% formic acid (30:70) at a flow rate of 1.0 mL min^{-1}. The sample injection volume was 20 μL, while UV detection was carried out at 294 nm.

2.3. Preparation of sorbent

SD was washed with water, 0.1 N HCl, and 0.1 N NaOH to clean the surface residual and bring in neutral, acidic, and basic surface activities. A 4 g of SD was weighed out in conical flask and 100 mL of 0.1 N HCl were added and placed in shaker for 30 min at 120 rpm. After shaking, SD was filtered out and washed with deionized water till filtrates pH became neutral. Treated SD was oven-dried overnight at 80°C and kept in closed bottle for further use. The same steps were repeated using 0.1 N NaOH for basic treatment.

2.4. Optimization of ofloxacin removal by SD

The retention of ofloxacin on SD was conducted by batch adsorption experiments in a thermostated shaker keeping the temperature constant at 35°C.

Different amounts of SD were agitated with solution containing different concentrations of ofloxacin at pH values 2–9 for a period of 10–180 min at 120 rpm. The residual concentration of analytes was analyzed by HPLC. The % removal was calculated by Eq. (1).

$$\% \text{ removal} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

where C_0 is the initial concentration, and C_e is equilibrium concentration (μg L^{-1}). All experiments were carried out in triplicate in order to minimize the error.

2.5. Sample collection

Hospital wastewater samples were collected from outfall drain of four local hospitals of Hyderabad, Pakistan. Amber glass bottles were used to collect samples from each site. After immediate transfer to laboratory, samples were vacuum filtered using

0.45 μm filter paper. Samples collection, filtration, and enrichment were completed on the same day to avoid any loss of ofloxcin in analysis.

2.6. Synthetic wastewater

Synthetic wastewater was prepared by mixing various nutrients, minerals, etc. using reported composition [15].

2.7. Solid-phase extraction

The solid-phase extraction was performed on Visiprep® Solid-Phase extraction system fitted with mini vacuum pump (Supleco, Bellefonte, PA, USA) utilizing Oasis® HLB cartridges 60 mg 3 mL^{-1} (Waters, Milford, USA) using reported method [16].

2.8. Mathematical and statistical procedure

Multi-variant sorption optimization was performed using Draper-Lin small composite design. The design contained 18 batch experiments; each experiment was performed at the different levels of independent variables. The range and level of independent variables are summarized in Table 1. Statgraphics Centurion (XVI) from Statpoint Technologies, Inc., USA was used for all calculations of CCD.

3. Results and discussion

3.1. Removal optimization by factorial design

Most of the methods reported so far have used the traditional uni-variant sorption optimization in which one factor is optimized at a time, keeping all other parameters at fixed values. In this type of optimization methodology, the effect of interaction terms cannot be studied which could lead to erroneous results. Another disadvantage of traditional sorption optimization is that it requires large time to carry many experiments for each variable and its cost is usually high. RSM on the other hand studies the effect of all parameters simultaneously on removal, therefore can consider interaction effects of parameters on each other which could lead to more reliable results.

RSM is a collection of mathematical and statistical techniques for empirical model building. By careful design of experiments, the objective is to optimize a response (output variable) which is influenced by several independent variables (input variables). The application of RSM to design optimization is aimed at reducing the cost of expensive analysis methods (e.g. finite element method or CFD analysis) and their associated numerical noise [17]. RSM have been successfully employed in various fields of analytical chemistry to minimize the number experiments [18]. In this study, RSM model with minimum number of experiments were designed and validated by fitting computational values with experimental values. The following section details the discussion on optimization of sorption process through this model.

Table 1
Levels of sorption parameters used in experimental design for ofloxacin removal

		Coded levels		
Independent variable		−1	0	+1
Amount (mg)	A (X_1)	10	30	50
Concentration (μgL^{-1})	B (X_2)	10	55.5	100
pH	C (X_3)	2	5.5	9
Time (min)	D (X_4)	10	95	180

3.2. Statistical analysis and model validation

Draper-Lin composite design was used to correlate observed and predicted % removal of ofloxacin from the aqueous solution. Both experimental and predicted values for the design of 18 experimental runs are summarized in Table S1. Correlation coefficient of 0.999 was observed for experimental and predicted removal for all three treated sorbents. The validity of linear equation for proposed model was tested by plotting a residual graph. A residual plot is a graph that shows the residuals on the vertical axis and the independent variable on the horizontal axis. The residual plots of all three sorbents (Fig. 1(a–c)) show a fairly random pattern with scattered values around the axis. Random dispersion of values around the horizontal axis validates the fitness of linear regression model.

In order to determine whether the calculated effects were significantly different from zero, Student's t-test for 95% confidence level and eight degrees of freedom were employed. The t-values found were 2.76, 1.77, and 1.98 for SD HCl, SD NaOH, and SD water, respectively. The evaluations are illustrated by means of Pareto charts in Fig. 2(a–c). The vertical line indicates the minimum statistically significant effect magnitude for a 95% confidence level. The values shown in the horizontal columns are Student's-test values for each effect. All the values presenting an absolute value higher than the given t-value, which are located right of the line, are significant. Positive and negative signs show the direct and inverse relationship of each parameter with removal of ofloxacin

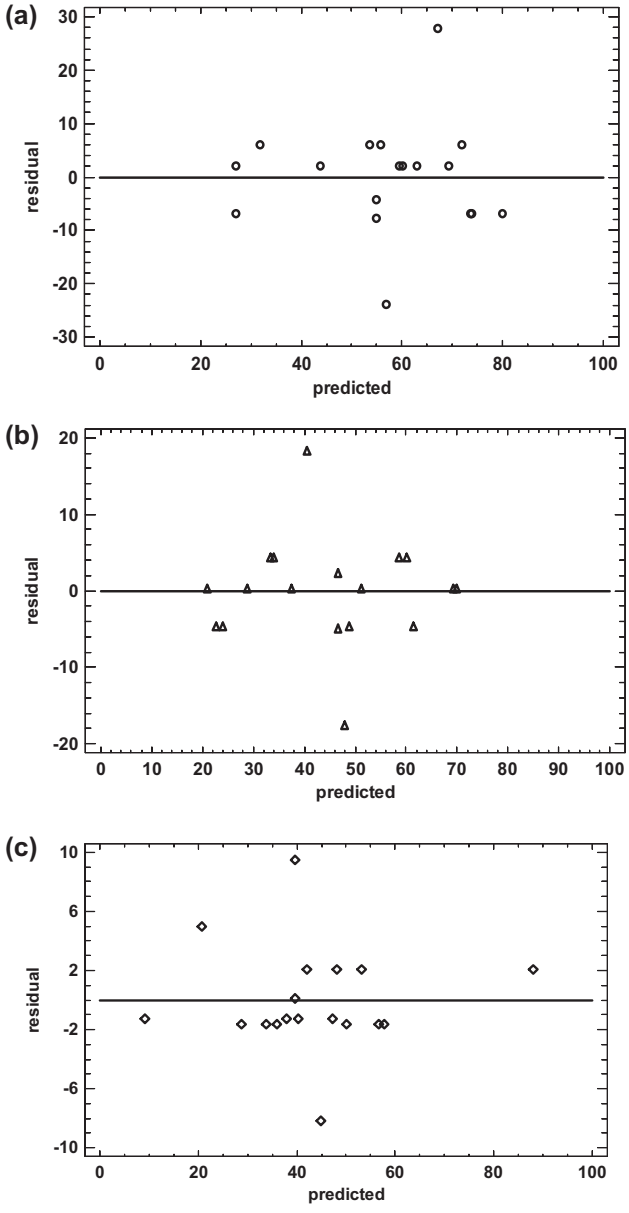

Fig. 1. Residual plot for removal of ofloxacin onto treated SD (a) HCl, (b) NaOH, and (c) water.

e.g. pH and time have positive significant effect on removal of ofloxacin (Fig. 2(a)). Concentration has negative impact on removal in the case of NaOH and water treated sorbents, however non-significant positive impact was observed in case of HCl-treated sorbent. Moreover, amount of sorbent have significantly positive impact on the removal for all three treated sorbents. Analysis of variance on these pareto charts showed p values lower than 0.05 for all parameters and sorbents other than concentration (p, 0.1007) in case of HCl-treated sorbent. The values of p lower than 0.05 shows the significance of these parameters for removal of ofloxacin.

Fig. 3(a–c) shows the effect of pH, concentration, amount of sorbent, and contact time on the removal of ofloxacin. These figures are generated by Statgraphics software applying Dapper-Lin composite design as mentioned earlier in the text. It can be seen from the figure that the removal increases with an increase in pH of the sorbate solution in case of HCl- and NaOH-treated sorbents. Adsorption is either a diffusion control, charge driven, or combination of both phenomena. SD is a porous material and is mainly composed of crude fiber followed by acid detergent, fiber that contains cellulose and lignin, protein and ash. All these components are active ion exchangers due to the presence of amine, carboxylic moieties etc. [19]. At pH values less than 3, the carboxylic groups become protonated and thus, are no longer available to attract positively charged ions from solution. When the pH is greater than 4, the carboxyl groups are deprotonated, therefore negatively charged and able to bind the positively charged ions. Ofloxacin is positively charged at pH lower than 6 and negatively charged above pH 7.2 [20]. The pH behavior (Fig. 3(a)) shows that the removal of ofloxacin by saw dust is not predominantly charge driven phenomena, therefore it may be suggested that the phenomena is governed by diffusion of ofloxacin molecule into the pores of saw dust.

The optimum sorption conditions determined from mathematical model were validated by conducting sorption experiment at optimum conditions. Table 2 shows a good agreement between the calculated and the predicted values for the removal of ofloxacin in all cases. However, the efficiency of acid-treated sorbent was relatively better than the base- and water-treated sorbent; therefore, acid-treated sorbent was further characterized to calculate the sorption efficiency.

3.3. Adsorption equilibrium studies

An important criterion in selecting a suitable adsorbent is their adsorption capacities. Adsorption isotherm study provides fundamental physiochemical data for evaluating the adsorption capacities of an adsorbent. Therefore, the equilibrium studies were carried out at varying initial concentration of ofloxacin and the data obtained was subjected to Langmuir, Freundlich, and D–R isotherm equations.

$$\frac{1}{q_e} = \left(\frac{1}{K_L q_{max}}\right)\frac{1}{C_e} + \frac{1}{q_{max}} \quad (2)$$

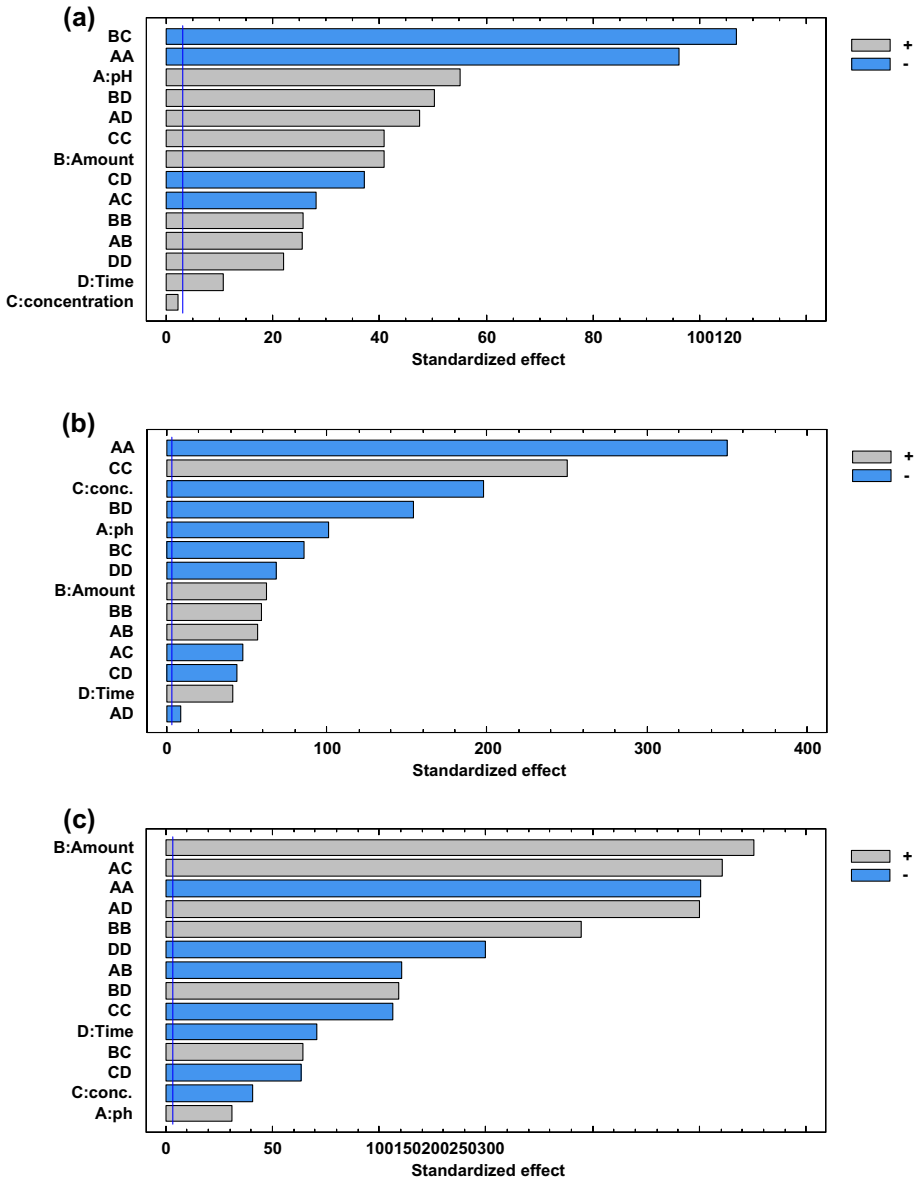

Fig. 2. Pareto charts for removal of ofloxacin onto treated SD (a) HCl, (b) NaOH, and (c) water.

$$\log\ q_e = \log K_F + \frac{1}{n}\log\ C_e \tag{3}$$

$$\ln q_e = \ln K_{D-R} - \beta\varepsilon^2 \tag{4}$$

where q_e is the amount of ofloxacin adsorbed onto the surface, C_e is the equilibrium concentration of ofloxacin in solution, q_m, K_F, and K_{D-R} are Langmuir, Freundlich, and D–R maximum adsorption capacity, respectively. K_L is the constant related to the binding energy of solute, $1/n$ is Freundlich constants representing adsorption intensity. ϵ is Polanyi potential and is equal to RT ln $(1 + 1/C_e)$, T is temperature, and R is general gas constant; β is related to the mean free energy of adsorption per mole of the adsorbent when it is transferred from infinite distance in the solution to the surface of the solid. Table 3 compiles the capacities and isotherm constant values obtained from the linear equation. The essential characteristic of Langmuir isotherm can be expressed in terms of dimensionless constant separation factor R_L which is defined as:

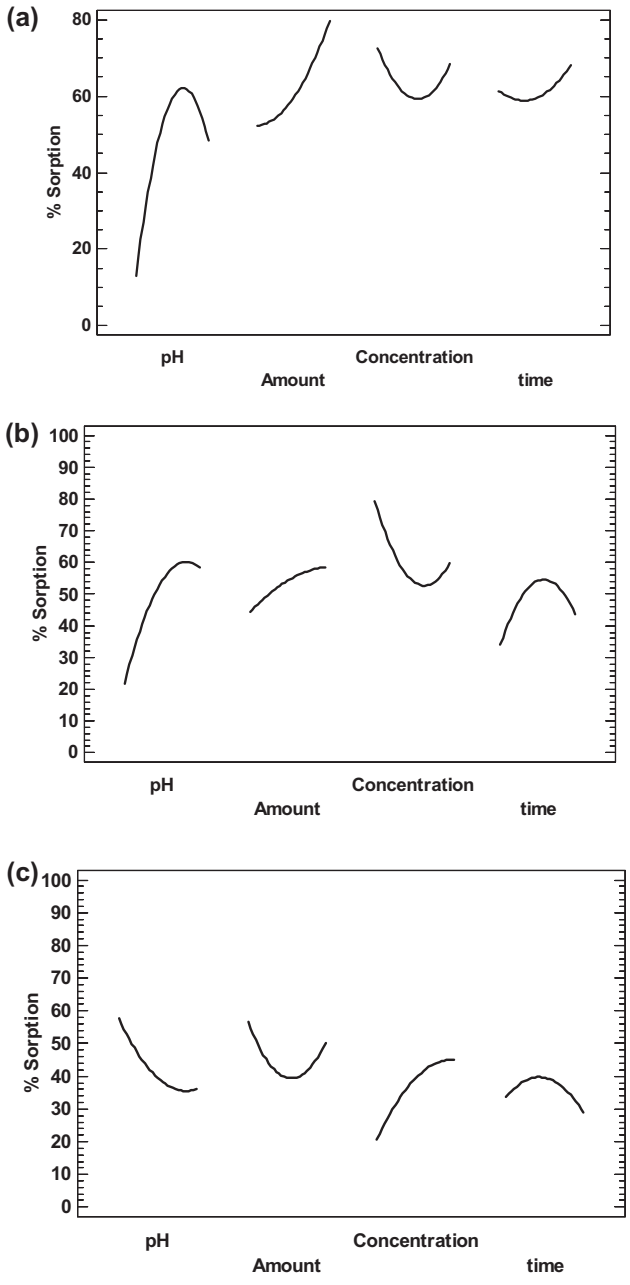

Fig. 3. Main effect charts for removal of ofloxacin onto treated SD (a) HCl, (b) NaOH, and (c) water.

$$R_L = \frac{1}{1 + (K_L C_i)} \tag{5}$$

According to the value of R_L, the isotherm shape can be interpreted as $R_L > 1$, unfavorable; $R_L = 1$, linear; $R_L = 0$, Irreversible; and $0 < R_L < 1$ favorable [21]. R_L values listed in Table 3 are less than 1 and greater than zero showing the favorable nature of adsorption. The values of energy of adsorption calculated from D–R isotherm found 12.9 K J mol^{-1}.

3.4. Kinetics of adsorption

To investigate the mechanism of adsorption of ofloxacin on treated SD adsorbent, the kinetic study was carried out at different time intervals from 1 to 195 min. Keeping other parameters at their optimum values (Table 2). Three kinetic models namely pseudo-first-order, pseudo-second-order and Morris–Weber were used to test the experimental data using Eqs. (6)–(8), respectively.

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{6}$$

$$\frac{t}{q_t} = \frac{1}{k q_e^2} + \frac{1}{q_e} t \tag{7}$$

q_e and q_t (mg g^{-1}) are the adsorption capacities at equilibrium and at time t, respectively. K_1 (min^{-1}) is the rate constant of pseudo-first-order adsorption, k is the equilibrium rate constant for second-order rate equation

Intraparticle diffusion (Morris–Weber) model [22] was used to study the mass transfer resistance on the binding of ofloxacin to the sorbent using Eq. (8):

$$q_t = K_d \sqrt{t} + C \tag{8}$$

where q_t is sorption capacity of ofloxacin on sorbent at time t (mg g^{-1}), K_d intraparticle diffusion rate constant (mg g^{-1} min$^{0.5}$), and C intercept which gives the idea of thickness of the boundary layer. Experimental data followed the equation with the correlation coefficient of 0.95. Linear portion of the plot did not pass through the origin indicating that intraparticle diffusion is not the only rate-limiting step [23]. It supports the idea of complex sorption mechanism with simultaneous Intraparticle diffusion as well as surface adsorption phenomena. Table 4 compiles the data of all three models for adsorption of ofloxacin onto HCl treated SD. The experimental value of q_e and the q_e calculated from the pseudo-second-order kinetic model were very close to each other, also, the calculated correlation coefficients, R^2 obtained from pseudo-second-order kinetic model were closer to unity for than those for the pseudo-first-order kinetics. These suggested that the pseudo-second-order adsorption mechanism is predominant.

Table 2
Optimum predicted parameter values and model validation

			Optimum value (*P)			% Removal (*P)			% Removal (*E)		
Factors	Low	High	HCl	NaOH	Water	HCl	NaOH	Water	HCl	NaOH	Water
Amount	10	50	50	10	50	100	76.66	91.4	95.8	75.98	90.92
pH	2	9	7.5	8.9	3.8						
Con.	10	100	10.0	40	48						
Time	10	180	150	180	70						

P = Predicted.
E = Experimental.

Table 3
Langmuir, Freundlich, and D–R sorption isotherm parameters for removal of ofloxacin onto HCl-treated SD

Langmuir				Freundlich			D–R		
Q (mmol g^{-1})	$b \times 10^5$ (mol L^{-1})	R_L	R^2	A (mmol g^{-1})	$1/n$	R^2	X_m (mmol g^{-1})	E (kJmol^{-1})	R^2
0.047	1.04	0.064–0.579	0.969	3.9	0.471	0.992	0.23	12.9	0.961

Table 4
Kinetic parameters for removal of ofloxacin onto HCl-treated SD

Pseudo-first-order			Pseudo-second-order			Moris–Weber	
K_1 (min^{-1})	q_e (mg g^{-1})	R^2	K_2 (μg g^{-1} min^{-1})	q_e (mg g^{-1})	R^2	K_d (μg g^{-1} min^{-1})	R^2
0.0152	5.55	0.924	0.0073	10.07	0.997	0.24	0.950

3.5. Thermodynamics

Thermodynamic study helps in estimating the feasibility of the sorption process [24]. The effect of temperature on the sorption of ofloxacin onto HCl-treated SD was studied in the range of 25–50°C under optimum conditions. A linear plot was obtained by plotting ln K_C against $1/T$ (T in K). The values of ΔH, ΔS, and ΔG were estimated using the relationships (Eqs. (9)–(11)).

$$K_c = \frac{F_e}{1 - F_e} \tag{9}$$

$$\ln K_c = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \tag{10}$$

$$\Delta G = -RT \ln K_C \tag{11}$$

where F_e is the fraction of ofloxacin sorbed at equilibrium. From the slope and intercept of the plot, values of $\Delta H = -40.5 \pm 1.63$ kJ mol^{-1}, $\Delta S = 119 \pm 5.62$ J mol^{-1} K^{-1}, and ΔG 303 K $= -6.28 \pm 0.11$ KJ mol^{-1} have been estimated with a correlation factor of 0.95. The negative values of ΔH and ΔG indicate the exothermic and spontaneous nature of the sorption.

3.6. Application of removal process

The real water samples were analyzed using reported procedure by spiking 100 mL of sample with 100 ng mL^{-1} of IBP. All the samples (neat and spiked) were cleaned up prior to chromatographic determination using solid-phase extraction. In order to establish the reliability of the reported method by Gros et al. [16] for extraction of ofloxacin, recovery experiments were carried out. Apparent recoveries, calculated as the ratio of the measured concentration of standards

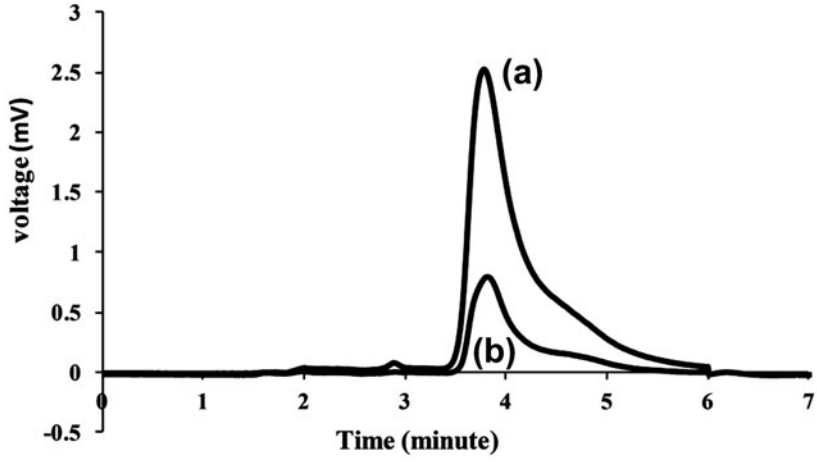

Fig. 4. HPLC chromatogram for spiked hospital wastewater sample (a) ofloxacin (10 μg mL^{-1}) and (b) after removal.

Table 5
Removal of OFLX in hospital wastewater water samples followed by SPE

Spiked sample[a]	% Removal
Sample A	85.4
Sample B	89.0
Sample C	87.3
Sample D	84.6

[a]Each sample was spiked with 100 ng mL^{-1} prior to preconcentration step.

levels to the spiked synthetic wastewater (expressed as percentage). For recovery, known amounts of ofloxacin added whose concentration after pre-concentration reached at 1, 5, and 10 μg mL^{-1}; the observed recoveries were 77%, 84%, and 94%, respectively.

Fig. 4 shows a chromatograph of real water sample and water sample spiked with standard ofloxacin. The obtained results are shown in Table 5 which shows that removal efficiency was in the range of 84.9–89%. The presence of IBP found in ng mL^{-1} level in nearly all of the samples which is higher as compared to earlier reports, mainly due to inefficient waste treatment plants in locality.

4. Conclusion

In this study, SD was treated with water, HCl, and NaOH, and removal of ofloxacin was optimized using RSM. Mathematical modeling successfully reduces the number of experiments for optimization process with reliable results. Optimization experiments showed that acid-treated SD was better for the removal of ofloxacin than that of water- and alkali-treated SD. Kinetic equations predicted a complex nature yet efficient sorption process. Thermodynamic studies indicated the spontaneous and exothermic nature of the sorption process indicating the infield utilization of this material without any energy requirements.

Supplementary material

The supplementary material for this paper is available online at http://dx.doi.10.1080/19443994.2015.1006825

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