A study on the removal of prednisone from aqueous solutions by adsorption onto a vegetal activated carbon

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ABSTRACT

This study evaluated the prednisone removal from aqueous solutions using adsorption by an activated carbon of vegetal origin (VAC). A central composite rotatable design (CCRD) and the response surface methodology (RSM) were used to verify the influence of the parameters: pH, adsorbent dose and prednisone concentration in a batch adsorption process. Among the analyzed parameters, only the adsorbent dose and the prednisone concentration were statistically significant ($\alpha = 0.05$) and the critical values obtained were adsorbent dose: 1.87 g/L, pH 7.56 and prednisone concentration: 3.66 mg/L with 77.51% of prednisone removal by VAC. The kinetic study of the adsorption of prednisone reached the equilibrium in 4 h. The pseudo-first-order model described adequately the kinetics data behavior. The equilibrium experimental data obtained at different temperatures showed that the VAC has a maximum adsorption capacity of 18.04 mg/g at a temperature of 30 °C. The prednisone removal decreased by the increasing temperature and the Langmuir isotherm well described the experimental data ($R^2 > 0.98$). Thermodynamic results shown that the prednisone removal of aqueous solutions by VAC is spontaneous and favorable process.

Key words | adsorption equilibrium, adsorption kinetics, experimental design, prednisone, thermodynamics, vegetal activated carbon

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INTRODUCTION

At a global level, it is estimated that at least half of the pharmaceutical wastewater generated by the industries is discharged into the environment without any treatment. The presence of pharmaceutical contaminants in the environment is considered potentially dangerous even at low concentrations. Therefore, the study of the effects of pharmaceutical waste in the environment is complex, being hampered by the large numbers of variables that influence the resulting toxicity (Monteagudo *et al.* 2013).

Researchers reported very high levels of pharmaceuticals in the effluent of a wastewater treatment plant (WWTP) near Hyderabad, India. They showed that as little as 0.2% of the effluent can result on a reduction of 40% of growth rate of tadpoles, but the underlying mechanisms of toxicity are unknown (Carlsson *et al.* 2009). Among the pharmaceuticals found in nature, prednisone has often been detected. Prednisone residues were found in the rivers of Catalonia (Spain) at concentrations ranging from 21 to 285 ng/L (Herrero *et al.* 2012). In France, prednisone was found at the concentration of 300 ng/L in effluent from a WWTP (Creusot *et al.* 2014) and in Arizona (USA) at the concentration of 20 ng/L in the effluent of a WWTP (Anumol *et al.* 2013).

Prednisone ($C_{21}H_{26}O_5$, molar mass: 358.434 g/mol, pKa: 12.58, formal charge: 0) is a glucocorticoid that is widely used in medicine due its low cost and for having the glucocorticoid and mineralocorticoid activity (Zhai *et al.* 2016). Although prednisone is highly prescribed, it has a wide variety of adverse effects in humans, such as adrenal atrophies, gastrointestinal bleeding, ulcer, diabetes, glaucoma, systemic reactions, and endocrine reactions, among others (Goyal & Bishnoi 2009).

The presence of pharmaceuticals residues in WWTP effluents and in aquatic environments indicates that the

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conventional wastewater treatments are not completely efficient for the removal of these kinds of residues.

Adsorption process using activated carbon as adsorbent has been widely used for the removal of bio-resistant organic materials residues in effluents due to the simplicity of the process operation, high efficiency, relatively low cost and the capacity of regeneration of the adsorbent (Ghafoori *et al.* 2014).

Adsorption is a mass transfer phenomenon that can occur by two mechanisms (physical and/or chemical adsorption); several factors can influence the process such as temperature, pH and physicochemical characteristics of the adsorbate (Dabrowski 2001). Thus, the study of the experimental factors influence on the adsorption process using a statistical approach is one of the first steps to develop an adsorption process in an efficient way with cost minimization.

The study of adsorption kinetics, and isotherms and thermodynamics are also essential requirements to obtain relevant information on the design and analysis of an adsorption process, since the kinetics describe the adsorption behavior over time, the isotherms describe the adsorption equilibrium and thermodynamics describe the adsorption mechanism.

In this context, the objective of this study was to evaluate the adsorption of prednisone onto a commercially activated carbon. The evaluation of operational parameters of the process (pH, adsorbent dose and initial drug concentration) was promoted by using a central composite rotatable design (CCRD). The equilibrium and adsorption kinetics studies were performed at different temperatures and in addition, a thermodynamic study was carried out to better understand the mechanism of the adsorption process.

METHODS

Adsorbent preparation and characterization

The adsorbent material used was the commercial vegetal activated carbon (VAC) (average diameter size of 1.40 mm) provided by a Brazilian company, the precursor of the VAC was the coconut shell. The material was washed with running water to remove grime followed by successive rinsing with distilled water. Afterward, the carbon was dried in a drying oven for 72 h at 70 °C. Afterwards, the VAC was stored for later use in experiments.

pH_{PZC}

Point of zero charge (pH_{PZC}) is the pH at which the adsorbent surface acquires zero charge. The '11 point scale' was used to determinate the pH_{PZC} of VAC (Regalbuto & Robles 2004). The experiments were performed by placing 0.5 g of VAC in contact with 100 mL of NaOH or HCl solutions under different pH conditions (1, 2, 3, 4, 5, 6, 8, 9, 10, 11, 12) at stirring speed of 160 rpm and 30 °C in an orbital shaking incubator (TECNAL TE-424). After 24 h, the final pH of the solutions was measured. The experiments were performed in duplicate and the data were represented using the OriginPro 2015 software.

Fourier transform infrared spectroscopy (FTIR)

The FTIR spectroscopy can determinate the vibration frequencies of the functional groups present in the activated carbon surface. The FTIR spectra of the samples were recorded between 4,000 and 650 cm^{-1} in a Perkin Elmer, Frontier FTIR Spectrum 100S spectrometer. The spectra were obtained using the attenuated total reflection (ATR) method with 40 scans applying a torque of 79 N with the articulated arm.

Prednisone solutions: preparation and quantification

The prednisone solutions used in the experimental runs were obtained by the dilution of a stock solution of 10 mg/L pharmaceutical concentration. The stock solution was prepared with prednisone (United States Pharmacopeia (USP) standard reference, purity ≥98%) provided by Prati-Donaduzzi (Brazil). The quantification of the initial and final concentration of prednisone solutions in the experiments were measured by ultraviolet-visible spectrophotometry (UV-Vis, Shimadzu UV-1800 Model), at wavelength of 248 nm, where the maximum absorbance was observed.

Evaluation of operational conditions of prednisone adsorption by VAC

A CCRD 2^3 was created with Software Statistica (ver. 8.0) for experimental design and data analysis. The three independent variables were adsorbent dose, pH and initial concentration of prednisone and the prednisone removal (%) was selected as the response parameter. The experiments proceeded according to the levels presented in Table 1. The CCRD 2^3 matrix consists of eighteen experiments: eight experiments are for the factorial design indicated by the lower (−1) and major (+1) levels, six experiments for the axial points (two for each variable) indicated by the levels (−1.68) and (1.68) and four replicates at the central point (0).

Table 1 | CCRD coded and real levels of prednisone adsorption onto activated carbon

	Levels				
Variable	**−1.68**	**−1**	**0**	**1**	**1.68**
X_1: Adsorbent dose (g/L)	0.20	0.41	1.0	1.59	2
X_2: Initial pH	3.0	4.62	7.0	9.38	11
X_3: Prednisone concentration (mg/L)	2.0	3.62	6.0	8.38	10

The conditions used in the experiments were: 50 mL of pharmaceutical solution, temperature of 30 °C and stirring speed of 160 rpm for 24 h in an orbital shaking incubator (TECNAL TE-424). The amount of removed prednisone (%) by the adsorbent was calculated by Equation (1):

$$\text{Removal}(\%) = \frac{(C_0 - C_{eq})}{C_0} * 100 \quad (1)$$

where C_0 is the initial concentration of prednisone solution (mg/L) and C_{eq} is the concentration of prednisone solution at equilibrium (mg/L).

Equation (2), which is an empirical second-order polynomial model, considers the performance of the scheme.

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2, \quad (2)$$

where β_0 is the intercept, β_1, β_2 and β_3 are the linear coefficients, β_{11}, β_{22} and β_{32} are the quadratic coefficients, β_{12}, β_{13} and β_{23} are the interaction coefficients and Y is the prednisone removal (%).

The accuracy and overall capacity of the polynomial model described above were evaluated using the coefficient of determination (R^2) and the analysis of variance (ANOVA) using Statistica (version 8.0) with a significance level of 5% ($\alpha = 0.05$), plus the response surfaces were obtained.

Kinetics and isotherms of adsorption

Adsorption kinetics experiments were performed in duplicate at the best experimental condition obtained from CCRD (adsorbent dose, pH and prednisone concentration). All the kinetics tests were performed in an orbital shaking incubator (TECNAL TE-424) at a stirring speed of 160 rpm, 30 °C and 50 mL of prednisone solution. Samples were collected and quantified by UV-Vis at pre-established time intervals until 24 h of running the experiment.

Adsorption isotherm experiments were carried out by placing 0.02 g of adsorbent in contact with 50 mL of the prednisone solution in different initial concentrations (2, 4, 6, 8, 10, 20 and 50 mg/L). The experiments were performed at the natural pH of the solution (approximately 6.46) under stirring at 160 rpm until the equilibrium was reached for three different temperatures (30 °C, 35 °C and 40 °C). After 24 h, the supernatant sample was collected and the concentration of prednisone in solution was determined.

The amounts of the prednisone adsorbed by the adsorbent at a specific time ($q(t)$, mg/g) and in equilibrium (q_{eq}, mg/g) were calculated by Equations (3) and (4), respectively:

$$q(t) = \frac{(C_0 - C(t))V}{m} \quad (3)$$

$$q_{eq} = \frac{(C_0 - C_{eq})V}{m} \quad (4)$$

where $C(t)$ is the concentration of prednisone at a specific time and at equilibrium (mg/L); V is the volume of solution (L) and m is the mass of adsorbent (g).

Two kinetics models, the pseudo-first-order (Lagergren 1898) and pseudo-second-order (Ho & McKay 1999) were used to investigate the mechanism of adsorption of prednisone on VAC and are represented by Equations (5) and (6), respectively.

The Langmuir (Langmuir 1918) and Freundlich (Freundlich 1906) adsorption isotherms (Equations (7) and (8), respectively) described the prednisone adsorption by VAC at equilibrium. The parameters of the models were obtained fitting the models to the experimental data using the Maple 2015®, applying the non-linear simplex method and the objective function of the sum of square errors (observed-predicted)².

$$q(t) = q_{eq}(1 - e^{-k_1 t}) \quad (5)$$

$$q(t) = q_{eq} \frac{q_{eq} k_2 t}{q_{qeq} k_2 t + 1} \quad (6)$$

$$q_{eq} = \frac{q_{max} b_L C_{eq}}{1 + b_L C_{eq}} \quad (7)$$

$$q_{eq} = k_f C_{eq}^{1/n} \quad (8)$$

where k_1 is the pseudo-first-order adsorption rate constant (min^{-1}); k_2 is pseudo-second-order adsorption rate constant (g/mg·min); q_{max} (mg/g) is the maximum amount of prednisone removed by the adsorbent at equilibrium, b_L (L/mg) is the Langmuir parameter; k_f is the empirical parameter of Freundlich; $1/n$ is a dimensionless empirical parameter.

Adsorption thermodynamics

Thermodynamic parameters such as the standard Gibbs free energy (ΔG^o, kJ/mol), enthalpy (ΔH^o, kJ/mol) and entropy variation (ΔS^o, J/mol·K) associated to the adsorption process can be used to deduce the adsorption mechanism. These parameters were calculated using the following Equations (9) and (10):

$$\Delta G^0 = -RT \ln(b_L) \quad (9)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (10)$$

where R is the universal gas constant (8.314 J/mol·K) and T (K) is the solution temperature; b_L is the Langmuir constant (L/mol) obtained at the equilibrium study by fitting the Langmuir isotherm model to the experimental data.

RESULTS AND DISCUSSION

pH_{PZC}

The pH_{PZC} is used to understand the pH influence on the charge net of the adsorbent surface. When pH >pH_{PZC} the surface of the adsorbent acquires a negative net charge and, when pH <pH_{PZC}, the surface of the adsorbent presents positive net charge (Furlan *et al.* 2010). The results of pH_{PZC} obtained for the VAC are presented in Figure 1.

The surface of the VAC presented zero charge (pH_{PZC}) at pH 5.8 (Figure 1). Usually, the values of pH_{PZC} are diverse for the activated carbons since they depend on the source of the precursor material and the activation methodology. Hassan *et al.* (2014) found values of 7.8, 6.0 and 7.1 of pH_{PZC} for activated carbons produced from calcium alginate, coconut shell and carbon/alginate composite beads, respectively.

In this study, the final pH did not show a significant variation at the initial pH range from 4.5 to 10 (Figure 1); at this pH range the surface of the coal acts as a buffer where there is a balance of positive and negative charges.

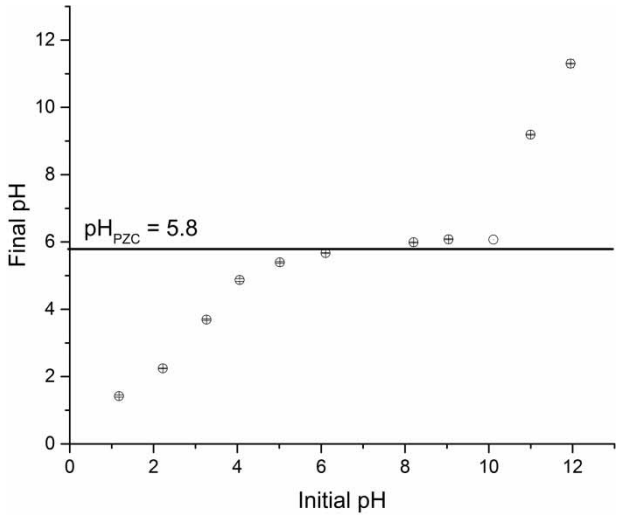

Figure 1 | Experimental data of pH_{PZC} for the adsorbent VAC (160 rpm, 30 °C, adsorbent dose: 1 g/L, contact time: 24 h).

Fourier transform infrared spectroscopy

The VAC infrared spectrum that provides information on the chemical structure of the adsorbent before the prednisone adsorption is presented at Figure 2.

The strong band obtained at 1,085 cm^{-1} (Figure 2) can be assigned to compounds with phosphorus oxide (V) or oxygenated functional groups in its structure (Jagtoyen *et al.* 1992). Broad band at 1,000–1,300 cm^{-1} is usually found with oxidized carbons and has been assigned to C–O stretching in acids, alcohols, phenols, ethers and/or esters groups, usually found in activated carbons obtained by chemical treatment with phosphoric acid (Toles *et al.* 1996; Puziy *et al.* 2002).

The band obtained at 1,561 cm^{-1} is probably due to stretching vibrations of the C = C groups (Fanning & Vannice *et al.* 1996; Puziy *et al.* 2002). Bands with peaks varying from medium to weak around 2,100 cm^{-1} are associated to the alkyne group (C ≡ C) (Pavia *et al.* 2001) and bands at 2,300 cm^{-1} are associated to the CH_3 group, while the 1,835 cm^{-1} bands correspond to the C = C-H

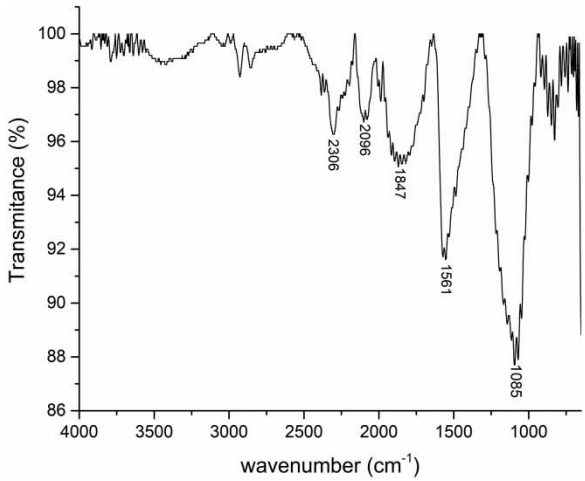

Figure 2 | Fourier transform infrared (FTIR) spectrum of the VAC adsorbent.

stretching (Pavia *et al.* 2001). Bands between 3,000 and 2,850 cm^{-1} can be assigned to compounds with aliphatic C-H groups and bands near 2,990 cm^{-1} correspond to symmetrical and asymmetric vibrations of C-H bonds belonging to the methyl and methylene groups (Guedidi *et al.* 2017). The spectra show a wide range of carbonaceous groups which is a characteristic of activated carbons. The C–H vibrations are probably due the loss of oxygen at the surface of the carbon material as well as the increase of phosphorus group content (1,085 cm^{-1}). Nevertheless, it is a characteristic of phosphorus and phosphor carbonaceous compounds present in the phosphoric acid activated carbons (Puziy *et al.* 2002).

Evaluation of operational conditions of prednisone adsorption by VAC

The matrix of the CCRD with the chosen variables to verify the removal of prednisone from aqueous solutions by the VAC adsorbent and the corresponding responses are shown in Table 2.

The results shown at Table 2 indicate that the VAC has a high potential of adsorption of prednisone from aqueous solutions, with 21.06% being the lowest removal obtained at run 9 and 87.55% being the highest removal obtained at run 8. Comparing runs 9 and 10, the increasing of adsorbent dose from 0.20 g/L to 2.0 g/L resulted in a prednisone removal increase of approximately 62%, indicating that the adsorbent dose has a positive effect on prednisone removal.

Table 2 | CCRD 2^3 matrix and results for the removal of prednisone from VAC

Run	X_1	X_2	X_3	Y (%)
1	−1 (0.41)	−1 (4.62)	−1 (3.62)	46.34
2	−1 (0.41)	−1 (4.62)	1 (8.38)	36.64
3	−1 (0.41)	1 (9.38)	−1 (3.62)	62.46
4	−1 (0.41)	1 (9.38)	1 (8.38)	21.17
5	1 (1.59)	−1 (4.62)	−1 (3.62)	79.55
6	1 (1.59)	−1 (4.62)	1 (8.38)	85.84
7	1 (1.59)	1 (9.38)	−1 (3.62)	77.71
8	1 (1.59)	1 (9.38)	1 (8.38)	87.55
9	−1.68 (0.20)	0 (7.0)	0 (6.0)	21.06
10	1.68 (2.0)	0 (7.0)	0 (6.0)	83.93
11	0 (1.0)	−1.68 (3)	0 (6.0)	83.75
12	0 (1.0)	1.68 (11)	0 (6.0)	47.26
13	0 (1.0)	0 (7.0)	−1.68 (2.0)	77.47
14	0 (1.0)	0 (7.0)	1.68 (10)	59.39
15 (C)	0 (1.0)	0 (7.0)	0 (6.0)	64.04
16 (C)	0 (1.0)	0 (7.0)	0 (6.0)	55.12
17 (C)	0 (1.0)	0 (7.0)	0 (6.0)	60.13
18 (C)	0 (1.0)	0 (7.0)	0 (6.0)	62.06

X_1: adsorbent dose (g/L); X_2: initial pH; X_3: prednisone concentration (mg/L);Y: prednisone removal (%); experimental conditions: 160 rpm; V = 50 mL; contact time = 24 h; T = 30 °C.

Comparing runs 1 and 3, the changing of pH from 9.38 to 4.62 resulted in a decrease of approximately 16% in the prednisone removal. In parallel, comparing runs 2 and 4, it was shown that changes in pH from 4.62 to 9.38 using identical dose of VAC (0.41 g/L) and prednisone concentration (8.38 mg/L) results in a decrease of approximately 16% in the prednisone removal, inferring that the pH variable has no proportional relation with the removal of the pharmaceutical. In runs 6 and 8, the changing in pH from 4.62 to 9.38 using an identical dose of VAC (1.59 g/L) resulted in removals of 85.84% and 87.55%, respectively, a difference of only 1.71%. The pH values within the pH range of 4.5 to 10 do not have a significant influence on removal of prednisone due to the buffer effect obtained by the surface of the adsorbent (Figure 1). The CCRD showed that the prednisone removal is facilitated in extremely acidic pH like is shown in run 11 (pH = 3.0; Y = 83.75%).

Prednisone is a weak acid (pKa: 12.5) whose molecule has a zero formal charge (Zhai *et al.* 2016). According to Henderson Hasselbalch's Equation (Hills 1973), when the pH of the solution equals the pKa of the solute, about 50% of the solute is dissociated and even a small change in the pH can drastically change the state of dissociation. At pH 11, the state of dissociation of prednisone is close to 50%, altering the equilibrium of electric charges of the system, which directly influences the adsorption process, and in this pH, the surface of the adsorbent assumes negative charge according with the pH_{PZC} results.

It is important to point out that the prednisone solution has a pH of around 6.46, a value close to the pH_{PZC} and close to the pH used at the central points of CCRD.

Table 3 shows the regression coefficients obtained by adjusting the variables to the quadratic model. The variable that most influenced the pharmaceutical removal was the adsorbent dose, and its quadratic contribution to the model was statistically significant at a significance level of 5% (Table 3).

The regression analysis of the experimental data using only the significant variables in the adsorption process resulted in the model represented by the quadratic equation

Table 3 | Regression coefficients of the independent variables and variable interactions

	Regression coefficients	Standard error	t(3)	*p*-value
Intercept	87.902	18.651	4.713	0.018*
(1) Adsorbent dose (L)	23.636	11.669	2.025	0.136
Adsorbent dose (Q)	−11.704	3.504	−3.340	0.044*
(2) pH (L)	−3.703	3.184	−1.163	0.329
pH (Q)	0.401	0.188	2.127	0.123
(3) Prednisone conc. (L)	−10.657	3.005	−3.546	0.038*
Prednisone conc. (Q)	0.584	0.188	3.097	0.053*
1 L by 2 L	−0.069	0.964	−0.072	0.947
1 L by 3 L	5.975	0.964	6.201	0.008*
2 L by 3 L	−0.619	0.239	−2.590	0.081

*Statistically significant for a confidence level of 5%.

(Equation (11)):

$$Y = 87.902 + 23.636\,X_1 - 10.657X_3 + 5.975\,X_1X_3 - 11.704X_1^2 \quad (11)$$

where Y is the prednisone removal (%) by VAC; X_1 is adsorbent dose (g/L), and X_3 is the initial concentration of prednisone solution (mg/L).

ANOVA results for the quadratic model with all variables are shown in Table 4. The critical Fisher-Value (F-Value) critical determined from Fischer-Snedecor table with $df_1 = 9$ and $df_2 = 3$ at confidence level ($\alpha = 0.05$) was found equal to 8.81. The model F-value, which is calculated as the ratio between model and residual mean square, was found equal to 53.31 what is 6.05 times higher than the critical F-value. This result shows a significant model regression at the experimental data of prednisone removal, with a determination coefficient (R^2) of 0.9178 indicating that the quadratic model can explain 91.78% of the variability of the experimental data. Therefore, the model is significant and predictive, since models that present values of F-value 4 to 5 times greater than the critical F-value are considered useful to make predictions (Box & Wetz 1973).

The regression of the model to the experimental data did not show a lack of fit (p-value > 0.05) indicating that the variation of the sample around the regression curve is given by the random error due to the variation of the replica observations, indicating that the model can efficiently describe the experimental data. The residual analysis had shown that the quadratic model is appropriate to represent the experimental data since the residuals are normal and independently distributed with a mean of 0 and constant variance.

The response surface methodology (RSM) was applied to evaluate the interaction between the variables in the prednisone adsorption process. The results are shown in Figure 3.

Figure 3(a) and 3(b) show the prednisone removal efficiency (%) is favored by increasing the adsorbent dose, since the greater the amount of adsorbent implies that are more sites available for the adsorption of the pharmaceutical. Figure 3(a) and 3(c) show that the lower the prednisone concentration, the greater the removal of prednisone in the process. The pH did not show significant statistical influence on the prednisone removal (%) by VAC, which is observed in Figure 3(a). Nevertheless, for studied conditions, the prednisone removal reached the minimal value when highly basic pH and high prednisone concentrations were used (Figure 3(c)).

The RSM did not show an optimal point of prednisone adsorption onto VAC. However, with the model fit, it was possible to predict critical values for the process variables (adsorbent dose: 1.87 g/L, pH: 7.56 and prednisone concentration: 3.66 mg/L), which provided the maximum removal of the pharmaceutical (77.51%).

The RSM model indicated that an adsorbent dose of 1.87 g/L and a pH of 7.56 would provide a greater removal

Table 4 | Regression coefficient of the independent variables and variable interactions

Source of variation	SS	df	MS	F-Value	Critical F-value	*p*-value
Regression	7,027.60	9	780.84	53.31	8.81	0.0038*
Residual	750.98	8	93.87			
Lack of fit	570.06	5	114.01	7.78	9.01	0.0609
Pure error	43.94	3	14.65			
Total	7,470.0	17				
R^2	0.9178					

SS: sum of squares; df: degrees of freedom; MS: mean square; *statistic significant in a confidence level of 95%.

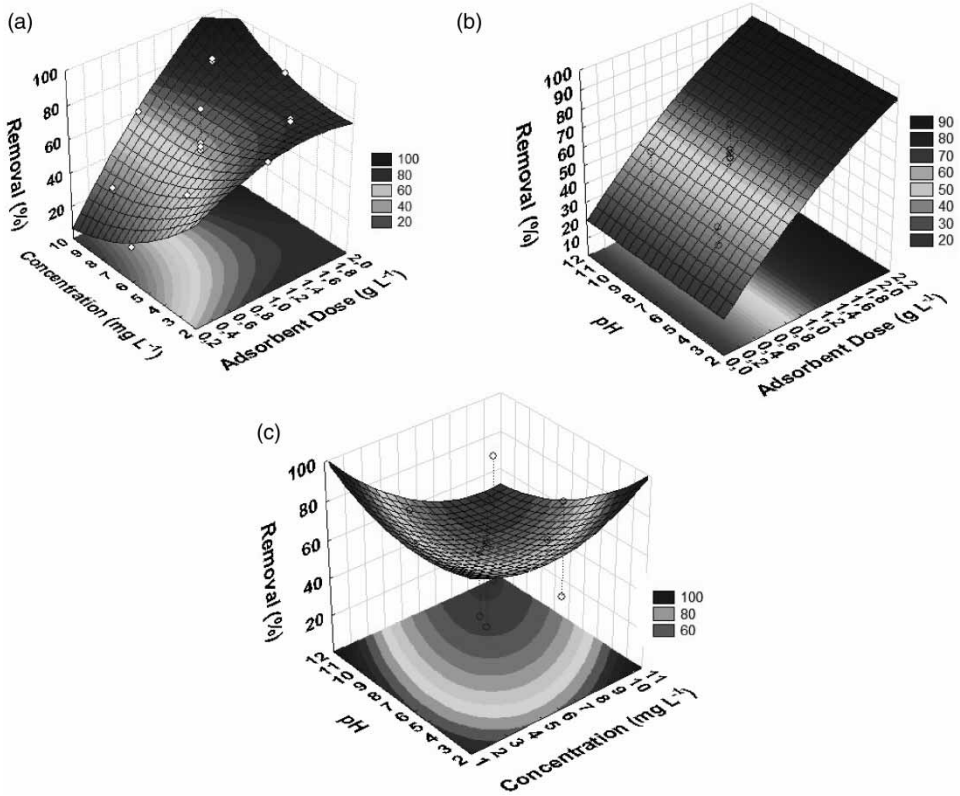

Figure 3 | Response surfaces representing the effects of the interactions between (a) adsorbent dose and concentration, (b) pH and adsorbent dose, (c) pH and concentration.

of prednisone; the results of CCRD showed that the adsorbent promoted a significant removal even at low dosages and the pH showed no significant influence on prednisone removal on range of 4.5 to 10. Thus, to proceed with the next experiments, the parameters used were: initial prednisone concentration of 10 mg/L, since it was the highest studied concentration; adsorbent dose of 0.41 g/L and pH of the solution of 6.46.

Kinetics and isotherms of adsorption

The kinetic plot (Figure 4) shows a fast prednisone removal at the initial period of 30 min on the adsorption process ($q_{eq} = 5.07$ mg/g) and, subsequently, the adsorption proceeded more slowly until equilibrium was reached at 4 h ($q_{eq} = 9.79$ mg/g), corresponding to a 40.94% removal. The reduction of the adsorption rate is associated with a gradual reduction of available active sites on the adsorbent surface.

The pseudo-first- and pseudo-second-order models were fitted to the experimental data and the fitted parameters are shown at Table 5. The evaluated kinetic models presented $R^2 > 0.972$ for the estimated parameters and allowed to infer that the pseudo-first-order model represents better

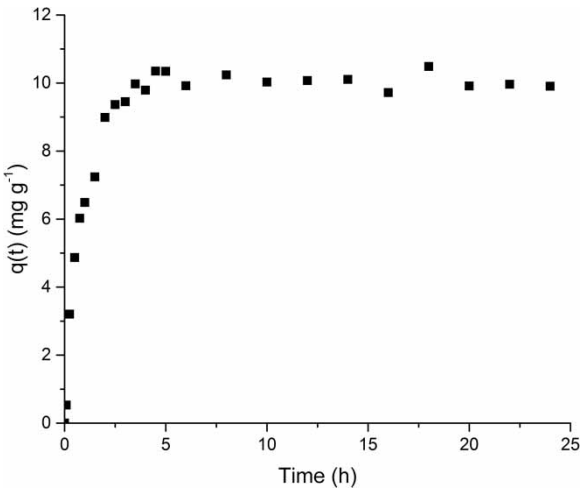

Figure 4 | Adsorption kinetics of prednisone in VAC (160 rpm, T: 30 °C, adsorbent mass: 0.02 g, V: 50 mL, C_0: 10 mg/L, pH 6.46).

the experimental data compared to the pseudo-second-order model, corroborating with the lower value of the objective function. With the adsorption rate constant (k_1) of 0.0166 min^{-1} the best fit of pseudo-first-order model implies that the process mass transfer resistance occurs due to the boundary liquid film around the adsorbent particles being

Table 5 | Kinetics models parameters of prednisone adsorption onto VAC

Pseudo-first-order			Pseudo-second-order		
k_1 (min^{-1})	R^2	F_{obj}	k_2 (g/mg·min)	R^2	F_{obj}
0.0166	0.993	0.43	0.0063	0.972	2.08

F_{obj}: objective function.

sufficiently small to be admitted the linear profile, which is an assumption of the pseudo-first-order model.

Tagliavini *et al.* (2017) obtained a similar result on the evaluation of the adsorption kinetics of estrone, estradiol, progesterone and testosterone in polymeric spherical activated carbon. At initial concentration of 100 ng/L, 260 rpm, pH 8, volume of 0.25 L, adsorbent dose of 0.01 g/L and temperature of 20 °C, the authors obtained the best fit of the pseudo-first-model ($R^2 > 0.97$) to the experimental data. The equilibrium was reached at approximately 6 h for all hormones and the equilibrium concentrations of 935, 1,039, 964 and 993 ng/g for estrone, estradiol, progesterone and testosterone, respectively.

The adsorption isotherms were carried out in order to obtain the maximum adsorption capacity of prednisone by the VAC adsorbent at temperatures of 30, 35 and 40 °C. The equilibrium coefficients of the Langmuir and Freundlich isotherms models at different temperatures, as well as their respective coefficients of determination (R^2) and objective function are presented in Table 6.

Table 6 | Equilibrium parameters of Langmuir and Freundlich isotherms of prednisone adsorption onto VAC

	Langmuir isotherm				Freundlich isotherm			
T (°C)	b (L/mg)	q_{max} (mg/g)	R^2	F_{obj}	k (L/g)	1/n	R^2	F_{obj}
30	0.142	18.04	0.99	0.01	2.60	1.84	0.94	0.23
35	0.208	12.55	0.98	0.04	2.56	2.18	0.92	0.26
40	0.217	10.47	0.98	0.05	2.15	2.17	0.89	0.32

The Langmuir isotherm model better fitted the equilibrium experimental data than Freundlich model presenting a $R^2 > 0.97$ and the lowest values of the F_{obj} (Table 6). The adsorption of the pharmaceutical by the adsorbent was favored at a temperature of 30 °C reaching a maximum removal capacity (q_{max}) of 18.04 mg/g at the pH of the solution (Table 6). The fact that the Langmuir isotherm resulted in a better fit to the experimental data may be associated with the model hypothesis that assumes homogeneous distribution of the active sites on the surface of the adsorbent.

Table 7 shows previous studies that used different activated carbons for adsorption of pharmaceuticals belonging to the same class of prednisone (glucocorticoid).

Although the activated carbons used in the presented studies are of different precursor materials, Table 7 shows that the maximum adsorption capacity (q_{max}) of prednisone by VAC is higher than other adsorbents for dexamethasone (Vadi *et al.* 2013) and steroids adsorption (Tagliavini *et al.* 2017). The prednisone molecule has a zero charge and can be considered a large molecule when compared to the steroids studied by Tagliavini *et al.* (2017). In addition, the present study obtained superior results with a shorter equilibration time and there was no need for pH adjustments, since the adsorbent acquires zero charge in the pH of the prednisone solution (approximately 6.46).

For a better understanding of the adsorption process mechanism, the thermodynamic studies are presented in Table 8.

In a physisorption process, the Gibbs free energy is between −20 and 0 kJ/mol while in chemisorption process the Gibbs free energy varies between −84 and −420 kJ/mol (Ahmad & Kumar 2010). For the prednisone, adsorption onto VAC the ΔG° was between −27.215 and −29.743 kJ/mol,

Table 7 | Previous studies of glucocorticoids or steroids adsorption by activated carbon

Pharmaceutical	Adsorbent	q_{max} (mg/g)	Experimental conditions	Reference
Dexamethasone	Spherical activated carbon	3.38	Magnetic stirring, adsorbent mass: 0.005 g, T: 25 °C; C_o: 4 a 12 mg/L, t: 10 min	Vadi *et al.* (2013)
Estrone Estradiol Progesterone Testosterone	Polymerbase spherical activated carbon	0.0126 0.0259 0.0297 0.0318	260 rpm, adsorbent mass: 0.002 g/L, V: 0.25 L; T: 20 °C; C_o: 100 ng/L to 1 mg/L, t: 26 h; pH: 8.	Tagliavini *et al.* (2017)
Prednisone	Vegetal activated carbon (VAC)	18.04	160 rpm, adsorbent mass: 0.2 g, T: 30 °C V: 0.05 L; C_o: 2 to 50 mg/L, t: 24 h	Present study

T: Temperature; t: Time; V: Volume.

Table 8 | Thermodynamic parameters of prednisone adsorption onto VAC (C_o: 2–50 mg/L, V: 50 mL, adsorbent mass: 0.02 g, 160 rpm)

T (°C)	T (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol·K)
30	303.15	−27.315	33.32	0.2
35	308.15	−28.743		
40	313.15	−29.320		

when the temperature increased from 303.15 to 313.15 K. According to the values of ΔG°, the process of prednisone adsorption in VAC is mainly physical and partly chemical. The negative Gibbs free energy values indicate that the adsorption process is spontaneous and favorable. The positive value of ΔH° (33.32 kJ/mol) indicates that the prednisone adsorption onto VAC is endothermic. The $\Delta S^\circ = 0.2$ kJ/mol·K shows the affinity of the adsorbent particles with the prednisone molecules and the increasing disorder at the solid–liquid interface during prednisone adsorption.

A similar result was obtained by Guedidi *et al.* (2017), authors performed thermodynamic studies for ibuprofen adsorption onto surface-modified activated carbon cloths. The authors obtained ΔG° values in the range of −1 to −6.75 kJ/mol and positive ΔH° values shown that the adsorption process had an endothermic nature.

Although it is expected that the adsorption process should be exothermic due to the energy released after the formation of the product of the interaction between solute and the adsorbent, the thermodynamic compensation justifies such an effect. It is verified that $T\Delta S^\circ > \Delta H^\circ$ in the temperature range of 30 to 40 °C, and the process is guided by spontaneity (entropy). This fact probably occurs due to the desolvation of both adsorbent and adsorbate (Ahmad & Kumar 2010).

CONCLUSIONS

In this study, the CCRD indicated that the critical prednisone removal efficiency (77.51%) by VAC occurred at pH 7.56; adsorbent dose of 1.87 g/L and initial solution concentration of 3.66 mg/L. The adsorbent dose and the prednisone concentration were the significant variables since the pH did not show statistical significance ($\alpha = 0.05$). The adsorption kinetics showed that the prednisone removal occurred rapidly in the first 30 min of contact, reaching the system equilibrium in 4 h, and the pseudo-first-order model best described the kinetics behavior ($R^2 = 0.993$). The experimental equilibrium data were best described by the Langmuir isotherm model ($R^2 > 0.98$) reaching a maximum adsorption capacity of 18.04 mg/g, 12.55 mg/g and 10.47 mg/g at 30 °C, 35 °C and 40 °C, respectively. The thermodynamic study indicated that the adsorption of prednisone onto VAC is spontaneous, favorable and predominantly physical process. The results indicate that the VAC can be an efficient adsorbent in prednisone removal from aqueous solutions and this process can be used in the final phase of the treatment of industrial effluents.

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AUTHORS' DISCLOSURE STATEMENT

No completion financial interest exists.

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