Removal of doxycycline hydrochloride from aqueous solution by rice husk ash using response surface methodology and disposability study

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Abstract

The huge demand and consumption of DOX, its incomplete metabolism, and complex behavior in atmosphere are causing a great ecological issue, which needs to be solved. In the present study, the suitability of rice husk ash (RHA) for the greater sorption efficiency of DOX antibiotic was investigated. Furthermore, disposability study of exhausted RHA was performed using solidification technique and leachate had undergone toxicity test to evaluate the DOX encapsulation ability. The central composite design under RSM was employed for the design of experiment and optimization of adsorption parameters. RHA was characterized using various techniques such as XRD, SEM (EDX), FTIR, BET, and zeta potential analysis. The influence of various adsorption parameters, like initial DOX concentration (C_0), RHA dosage (m), incubation-time period (t), and pH were examined on the performance in terms of DOX elimination % (X_1) and adsorptive capacity (mg/g) (X_2). At optimized conditions, the obtained X_1 and X_2 were 98.85% and 17.74 mg/g, respectively. Moreover, the kinetics data suited well to the pseudo-second-order model. Freundlich, Langmuir, and Redlich-Peterson (R-P) isotherm models were applied, out of which Langmuir model best performed under optimized conditions; $m = 5$ g/L, $t = 85.85$ min, DOX concentration = 89.73 mg/L, and pH = 6. The bacterial toxicity test of leachate confirmed complete encapsulation of DOX by solidification technique.

Keywords Rice husk Ash · Doxycycline hydrochloride · Adsorption isotherms · Diffusivity studies · Solidification and stabilization

Introduction

Pharmaceutically active compounds (PACs) and their complex metabolite forms are present in the H_2O cycle of the environment. It is extensively identified all over the globe, and the concentrations of PACs are examined in the ground and potable water specimen. These compounds fall into the emerging chemical class due to their significant consumption, broad reactivity, health hazards, and ecological risks (Sobsey and Bartram 2002). Antibiotics are classified in several categories like fluoroquinolones, trimethoprim, sulfonamides, and tetracyclines. Out of these, tetracyclines (TCs) are one of the highest consumed antibiotics for controlling various diseases due to their effective results (Saygili and Guzel 2016). Presently, antibiotics have been detected in influents and effluents of wastewater streams and almost 50–90% is in the form of metabolites (Li et al. 2013). Where, TCs were widely identified antibiotic ($\approx 80\%$) in the industrial and domestic drainage systems. Doxycycline hydrochloride (DOX) is an antibiotic that belongs to the tetracycline

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(TC) group (Kaur et al. 2021c). Due to its wide-ranging antibacterial function and effectiveness on gram-positive and gram-negative strain of bacteria, it has achieved more popularity than other TC antibiotics (Li et al. 2013).

Recently, DOX has been used with other drugs to minimize COVID-19-induced inflammation (Gupta and Rana 2020). Due to the complicated physicochemical behavior of DOX, it shows complex nature in the ecosystem. In proportion to its complicated structure and good solubility, DOX exhibits high residual toxicity in the aquatic environment. Due to the high solubility of DOX in water, it contaminates the water bodies and increases antimicrobial resistance of microorganisms (Kaur et al. 2021b). There is a need to find the suitable process for the removal of DOX present in the wastewater. Numerous processes (physical, chemical, biological, and advanced oxidation) have been employed for the elimination of DOX from wastewater. Due to energy-intensive nature and formation of toxic intermediates, most of these processes do not find its industrial application (Kaur et al. 2019a, b; Rani et al. 2021). On the other hand, adsorption is an operative technique at a large scale and is away from these drawbacks (Kaur et al. 2021d).

Few researchers have come out with the sorption of TCs with the help of different types of adsorbents like montmorillonite (Zhao et al. 2012), carbon nanotubes (Kim et al. 2014; Tang et al. 2014), graphene (Gao et al. 2012), mesoporous silica (Zhang et al. 2015), Fe_3O_4 (Ghaemi and Absalan 2015), and sea buckthorn biocarbon (Zhang et al. 2016). Most of them are associated with drawbacks like high cost, regeneration inability, and poor adsorption capacity. Very few adsorbents have been explored which provide efficient removal rate and good sorption capacity. On the other hand agri-residues are better options for adsorption of antibiotics due to their abundance availability, negligible cost, and good performance.

In the present study, RHA was selected as sorbent for the uptake of DOX from its aqueous solution. Rice husk is one of the highest produced agricultural waste materials that contains about 22–25.5% of their weight (Mohamed et al. 2015). It is used as fuel materials into the incinerators by various industries and the ash produced is called RHA. The worldwide rice husk production is approximately 545 million metric tons, whereas India alone generates approximately 18–22 million tons of rice husk annually (Srivastava et al. 2006). Therefore, huge amount of rice husk burnt or deposited as wastage creates various environmental and health-related problems (Kaur et al. 2021a; Naiya et al. 2009). So, there is a need to utilize this ash generated from incinerators. Moreover, because of a very high silica content (more than 80%), RHA has the exceptional ability to be used as an adsorbent. Due to its noble physical and chemical characteristics, many researchers have used RHA for the removal of various pharmaceutical compounds. Earlier, ofloxacin hydrochloride, paracetamol (Thakur et al. 2020),

ofloxacin (Kaur et al. 2021a), oxytetracycline (Andrade et al. 2020), and pyridine (Lataye et al. 2008) were adsorbed on RHA with high removal capacity.

The central objectives of this research study are as follows: (1) to measure the degree of removal of DOX using RHA as adsorbent (2) optimization of process parameters using RSM and evaluation of suitable kinetic and isotherm models (3) solidification/stabilization of exhausted RHA and bacterial toxicity analysis of leachate to evaluate the degree of encapsulation of DOX.

Experimental

Materials and characterization techniques

The RHA was purchased from the rural market of Patiala, India. It was cleaned using hot water and undergone drying for overnight at 70 °C temperature. After drying, it was screened, and the used particle size of RHA was 180–600 μm . Now, it was used as an adsorbent without any further treatment. The doxycycline hydrochloride (DOX) with chemical formula $\text{C}_{22}\text{H}_{25}\text{ClN}_2\text{O}_8$ and molecular weight 480.9 g/mol was obtained from Varav biogenesis Private Ltd. Himachal Pradesh, India.

The wastewater of DOX antibiotic was synthetically prepared in different concentrations, using deionized water. All the chemicals employed for this work were of analytical class. For maintaining the desired pH of DOX solution, 1–2 N H_2SO_4 and NaOH solutions were used. The spectrophotometric analysis of DOX solutions was performed at 345 nm wavelength, using UV–VIS spectrophotometer (model HITACHI U-2000). A Thomas Scientific incubator shaker was used for adsorption studies.

Rice husk ash characterization

Various characterization techniques were used to evaluate the morphological and chemical properties of RHA. The specific surface area was evaluated with the help of BET technique, and the pore volume (total) was evaluated at a relative pressure of about 0.95 in the presence of liquid nitrogen. The pore size was determined via Barrett–Joyner–Halenda (BJH) technique. The morphology of the activated carbon was inspected via scanning electron microscope and elemental composition has been obtained by EDX analysis (Hitachi S4800 HR-SEM, Germany).

The XRD (X-ray diffraction) pattern of RHA was evaluated by Bruker D8-Advance X-ray diffractometer (Bruker, Germany), at $2\theta = 10\text{--}90^\circ$ with Cu as the object and Ni as the filter media with $\lambda = 1.541 \text{ \AA}$ having $\text{K}\alpha$ radiations. It shows the specific interactions between the adsorbate and adsorbent. Moreover, the FTIR pattern was obtained with

the help of a spectrophotometer (Nicolet 6700 spectrometer, USA) amid 4000–400 cm^{-1} wavelength range at room temperature which represents different functional groups on the RHA surface before and after adsorption.

The point of zero charge (pH_{Pzc}) of the RHA was also evaluated, which facilitated in understanding the sorption mechanism of DOX on the RHA surface. Salt addition technique was used for this purpose. In this method, the deviation between the zeta potential values was estimated, and the point at which ΔpH becomes nil was measured as pH_{Pzc} of RHA. The pH_{Pzc} of RHA was determined by following the similar procedure reported earlier (Mahmood et al., 2011). For this purpose, eleven clean conical flasks of 100 mL capacity were taken and 40 mL of 0.1 M KCl solution was poured into each flask. The solution pH of different flasks were adjusted to different values ranging from 2 to 12 with the help of 0.1 M H_2SO_4 and 0.1 M NaOH as per requirement. Furthermore, 0.2 g of RHA sample was added into each flask and these flasks were placed in a rotary shaker for 24 h at room temperature and 200 rpm. After 24 h, the supernatant of each flask was taken out and its pH was measured. The difference between the initial and final pH was evaluated, and the point at which difference (ΔpH) is zero was considered as pH_{Pzc} of RHA. The pH_{Pzc} of RHA was evaluated as 8.1 and is shown in Fig. S1.

Experimental design and optimization of parameters

The sets of experiments for DOX adsorption on RHA were designed by applying Design-Expert software version13 (DX10). Full factorial design was used based on two levels with 8 axial points and 6 center points. The CCD model involves four varying parameters (initial concentration, time, pH, and adsorbent dose) whereas temperature and rotation speed remain constant throughout the experimentation. The ranges were setup like the following: DOX concentration (10 to 90 mg/L), adsorption duration (10 to 750 min), pH (2–10), and dosage of RHA (0.5–2.5 g/100 mL). Variables were coded with five different levels of CCD model (Table 1). These were observed as self-reliant sorption parameters, whereas (X_1) and (X_2) were designated as responses. The quadratic model was used to fit the experimental findings,

analysis, and optimization of adsorption parameters as given by Eq. (1).

$$X = \psi_0 + \sum_{i=1}^k \psi_i x_i + \sum_{i=1}^k \psi_{ii} x_i^2 + \sum_{i < j} \psi_{ij} x_i x_j + D_r \quad (1)$$

where ψ_0 is the constant coefficient of the model; ψ_i , ψ_{ii} , and ψ_{ij} represent as the linear interactive coefficients, quadratic, and second order constants. x_i and x_j are variables and D_r denotes to error. Furthermore, for the parameter interaction analysis, ANOVA (analysis of variance) was used. From the ANOVA table, the F and P values for both the responses, percentage removal, and capacity were attained. The validation of the quadric model was analyzed by various R^2 values. So it is concluded that model terms are significant with a confidence level of 95%. For optimizing both the responses, a multi-response optimization tool was used with a desirability function of RSM (Sangal et al. 2013).

Batch adsorption measurements and data analysis

In this work, initially, thirty experiments were designed to assess the relationship between dependent and independent variables created by CCD/RSM (Table 2). The fresh stock solutions of required concentrations were prepared daily using deionized water. The sets of experiments were performed under batch process followed by RSM-suggested experimental list. For every experiment, 100 ml DOX solution (of definite dose) was taken in 150-mL stoppered conical flasks and its pH was adjusted using the desired concentrations of acid/base solutions. The predetermined amount of RHA was added to the solution and it was agitated in an incubator shaker at 150 rpm and 303 K temperature. After a programmed time, mixtures of DOX and RHA were separated with the help of Whatman no.1 filter paper, and the remains were characterized for DOX content (C_e) using a dual-beam UV–visible spectrophotometer (HITACHI U-2000 model) at wavelength (λ_{max}) = 345 nm with the help of the calibration curve. The X_1 and X_2 responses of RHA were then examined using the following equations:

$$X_1 = \frac{(C_0 - C_f)}{C_0} \times 100 \quad (2)$$

Table 1 Different range of variables and levels of the design model

Factors	Variables	Range of actual and coded variables				
		(−2)	(−1)	(0)	(+1)	(+2)
A	pH	2	4	6	8	10
B	Dose (g/L)	5	10	15	20	25
C	DOX conc. (mg/L)	10	30	50	70	90
D	Time (min)	10	195	380	565	750

Table 2 Design of experimentation for the adsorption of DOX by RHA

Std	Run	pH	Dose (g/L)	DOX conc. (mg/L)	Time (min)	% DOX removal (X_1)	Adsorption capacity (X_2)
14	1	8.0	10.0	70.0	565.0	96.66	6.76
3	2	4.0	20.0	30.0	195.0	91.70	1.37
11	3	4.0	20.0	30.0	565.0	92.21	1.38
4	4	8.0	20.0	30.0	195.0	90.67	1.36
18	5	10.0	15.0	50.0	380.0	95.31	3.17
25	6	6.0	15.0	50.0	380.0	94.08	3.13
22	7	6.0	15.0	90.0	380.0	95.88	5.75
9	8	4.0	10.0	30.0	565.0	94.42	2.83
27	9	6.0	15.0	50.0	380.0	94.21	3.14
12	10	8.0	20.0	30.0	565.0	90.47	1.35
5	11	4.0	10.0	70.0	195.0	98.12	6.86
19	12	6.0	5.00	50.0	380.0	96.87	9.68
1	13	4.0	10.0	30.0	195.0	94.98	2.84
23	14	6.0	15.0	50.0	10.0	95.47	3.18
29	15	6.0	15.0	50.0	380.0	94.28	3.14
24	16	6.0	15.0	50.0	750.0	94.99	3.16
30	17	6.0	15.0	50.0	380.0	94.31	3.14
7	18	4.0	20.0	70.0	195.0	96.86	3.39
10	19	8.0	10.0	30.0	565.0	93.30	2.79
17	20	2.0	15.0	50.0	380.0	96.60	3.22
21	21	6.0	15.0	10.0	380.0	87.64	0.58
20	22	6.0	25.0	50.0	380.0	92.31	1.84
15	23	4.0	20.0	70.0	565.0	95.73	3.35
26	24	6.0	15.0	50.0	380.0	94.13	3.13
8	25	8.0	20.0	70.0	195.0	95.67	3.34
2	26	8.0	10.0	30.0	195.0	93.94	2.81
13	27	4.0	10.0	70.0	565.0	97.14	6.80
16	28	8.0	20.0	70.0	565.0	94.87	3.32
28	29	6.0	15.0	50.0	380.0	94.26	3.14
6	30	8.0	10.0	70.0	195.0	97.69	6.83

Similarly, the sorption capacity, q_e (mg/g) was determined as follows:

$$q_e = \frac{(C_0 - C_e)}{m} \times V \quad (3)$$

Here, C_0 and C_e denote the original and equilibrium DOX concentrations, C_f denotes the final concentration of DOX (mg/L), V is the sample volume (mL), and m (g) denotes the amount of RHA.

Solidification and stabilization (S/S) studies of DOX loaded RHA

The S/S is generically defined as a chemical and physical alteration technique for reducing the movement of contaminants from wastes by converting them into the chemically inert form. Among various S/S binders, cement-based

systems are usually evaluated due to its low cost, wide-ranging disposal, and adaptability (Bie et al. 2015). In this technique, the cementing material is mixed with contaminated solid and water and due to the rapid settling, a rigid structure is formed which develops strength in the mixture, and contaminants are bonded inside. So it is a process that makes an inert solidified complex structure that does not react further while changing the atmospheric conditions (Poon et al. 2004).

To detect the effect of binding agent on the leachability behavior of DOX, antibiotic carrying exhausted RHA and Portland cement were mixed with different adsorbent to cement ratios (Table 3). Furthermore, beads of around 2 cm diameter were prepared with the help of water and it was kept for 24 h in natural atmospheric condition. These beads were incubated at room temperature for 15 days in 100 mL distilled water and the water level was maintained in the testing beakers (Kaur et al. 2021a). After that, the

Table 3 Different used combinations of exhausted/loaded adsorbent (RHA-DOX) and cement for solidification study

Sample No	Mass of adsorbent+cement in mixture	Mass ratio of adsorbent to cement
1	1 g adsorbent + 5 g cement	1:5
2	2 g adsorbent + 4 g cement	1:2
3	3 g adsorbent + 3 g cement	1:1
4	4 g adsorbent + 2 g cement	2:1
5	5 g adsorbent + 1 g cement	5:1

sample (leachate) was tested for DOX concentration using UV–visible spectrophotometer at 345 nm and the encapsulation percentage was calculated using Eq. (4).

$$\text{Capsulation percentage} = \frac{(C_a - C_l)}{C_a} \times 100 \quad (4)$$

where C_a and C_l indicate the DOX amounts (mg/L) in RHA and leachate.

Cytotoxicity analysis

After completing the solidification and stabilization process, the toxic effects of different leachate samples were analyzed by adopting the agar cup process (Collier et al. 2006). The test was performed on Petri plates by agar cup method. Two microbial species, *E. coli* (EC) and *Bacillus subtilis* (BC), were restored in nutrient medium. Furthermore, Mueller and Hinton agar (MHA) media was used to examine the toxicity test and then spreading was done on petri plates through selected bacterial strains. Two to four wells were made per plate using a 0.5-mm sterilized cork borer, and a 0.25 µl of leachate sample was put into each well. For comparison purpose, DOX solution of different concentrations (0.1 to 10 ppm) was also put in few wells. After that, plates were kept in an incubator at 35 ± 0.1 °C for 24 h and the results were perceived.

Results and discussion

Characterization of the RHA

The FTIR spectra of DOX, fresh RHA, and DOX-loaded RHA are shown in Fig. 1. In DOX spectrum, the wide peak amid 3412 to 3667 cm^{-1} is dedicated to –OH groups. Sharp peaks at 1670 cm^{-1} and 1647 cm^{-1} represent to C=O and amide I groups, respectively. The absorption bands at 1617 cm^{-1} and 1581 cm^{-1} are particular for –COOH and amide II groups, respectively. Moreover, the vibration band at 1245 cm^{-1} is attributed to the amide III group. In RHA,

Fig. 1 FTIR spectra of RHA, DOX-RHA, and DOX

before the adsorption of DOX, the presence of a wide peak amid 3100 to 3700 cm^{-1} is recognized as the both free and H-bonded OH bands present on the exterior of RHA (Srivastava et al. 2006). In the spectrum, the predominantly noticeable peaks correlate with the Si–O, Si–OH, and Si–O–Si groups at regions 1095 and 795 cm^{-1} , respectively. According to the reported literature, the main component of RHA is silicon that exists in the form of SiO_2 . After the adsorption, many changes were observed in peak patterns and the vibration of DOX was observed in the loaded RHA sample. The distinctive absorption bands were diagnosed which were correlated with DOX at 1657 cm^{-1} , 1615 cm^{-1} , 1582 cm^{-1} , 1038 cm^{-1} , 769 cm^{-1} , and 598 cm^{-1} in the loaded sample. Moreover, shifting in peaks from 1095 to 1038 cm^{-1} and 795 to 769 cm^{-1} shows the deformation of Si–O, Si–OH, and Si–O–Si groups that points out that DOX antibiotic has been positively performed (Abou-Mesalam 2003).

XRD diffraction patterns (Fig. S2) of blank RHA showed SiO_2 , cristobalite, and Trydimite. On the other hand, some sharp and narrow peaks seen in the loaded sample at 2 theta 20.25 and 37.2 explain the amorphous nature of RHA due to the presence of SiO_2 and cristobalite. These were the deviations observed between blank RHA and loaded RHA adsorbent. The specific surface area of the DOX was evaluated by using the nitrogen adsorption–desorption method well established on the BET model at temperature 77 K in the presence of liquid nitrogen. As a result, the specific surface area and average BET pore diameter of adsorbent were evaluated as 32.6 m^2/g and 6.5 nm, respectively. Thus, it indicates the mesoporous nature of RHA due to $d < 20 \text{ \AA}$ and proves to be a suitable adsorbent for the sorption. The average particle size of the used RHA was found to be 146.3 µm. Moreover,

the SEM–EDX pattern of RHA and DOX-RHA is shown in Fig. 2. The particles have a well-arranged pattern on the external surface of RHA which is shown in Fig. 2a; the internal surface of particle is highly porous and fibrous in nature. Therefore, the existence of mesopores and macropores is supportive for the sorption of DOX molecules on their surface. Figure 2c represents that all the pores are filled with DOX adsorbate and it forms a well-structured network on the RHA surface. Furthermore, the EDX spectrum of both samples (Fig. 2b, d) indicates that the major constituents of RHA are silica and oxygen that are accumulated as SiO_2 . The main differences are seen in these both (Si and O) components and some other components were also found in lesser concentrations as shown in Fig. 2b, d.

Model suitability and statistical investigation

The experimental runs suggested by the CCD model of RSM were completed, and the responses (X_1) and (X_2) were calculated (Table 2). The statistical analysis results of experimental data were found using the variance of the ANOVA table generated by the RSM. It involves a sum of squares, F -value, probability values, etc.; these were analyzed (Table 4) and it was recommended by the sum of squares (sequential model) that the quadratic model was the most suitable for the experimental data. The calculated

values of 52.36 and 25.11 were found for acceptable precision of both responses (X_1) and (X_2) individually. On the other hand, the model F -values for X_1 and X_2 were 148.87 and 37.17 as listed in Table 4.

Thus, it supported the value of the quadratic model. So, the final equations are given in the form of following second-order polynomial quadratic model:

$$X_1 = 99.52 - (1.61 \times \text{pH}) - (0.52 \times m) + (0.19 \times C) - (6.47 \times 10^{-3} \times t) + (0.11 \times \text{pH}^2) + (5.57 \times 10^{-3} \times m^2) - (1.42 \times 10^{-3} \times C^2) + (8.73 \times 10^{-6} \times t^2) - (0.01 \times \text{pH} \times m) + (3.06 \times 10^{-3} \times \text{pH} \times C) - (8.58 \times 10^{-5} \times \text{pH} \times t) + (3.20 \times 10^{-3} \times m \times C) + (1.07 \times 10^{-4} \times m \times t) - (5.15 \times 10^{-5} \times C \times t) \quad (5)$$

$$X_2 = 5.27 + (0.06 \times \text{pH}) - (0.78 \times m) + (0.15 \times C) + (6.62 \times 10^{-4} \times t) - (6.20 \times 10^{-3} \times \text{pH}^2) + (0.02 \times m^2) - (8.07 \times 10^{-5} \times C^2) - (9.01 \times 10^{-7} \times t^2) + (9.45 \times 10^{-5} \times \text{pH} \times m) - (4.595 \times 10^{-5} \times \text{pH} \times C) - (8.51 \times 10^{-7} \times \text{pH} \times t) - (5.02 \times 10^{-3} \times m \times C) + (7.72 \times 10^{-6} \times m \times t) - (2.99 \times 10^{-6} \times C \times t) \quad (6)$$

The close to unity values of R^2 , R_{adj}^2 , and R_{pre}^2 confirmed that the quadratic polynomial model to signify the

Fig. 2 SEM–EDX analysis of RHA and DOX loaded RHA (a, b, c, and d)

Table 4 ANOVA tables for the % DOX removal and capacity

% DOX removal (X_1)						Adsorption capacity (X_2)				
Source	Sum of squares	DF	Mean square	<i>F</i> value	Prob > <i>F</i>	Sum of squares	DF	Mean square	<i>F</i> value	Prob > <i>F</i>
Model	154.49	14	11.03	148.87	< 0.0001	116.42	14	8.32	37.17	< 0.0001
A	4.58	1	4.58	61.78	< 0.0001	4.491×10^{-3}	1	4.491×10^{-3}	0.020	0.8892
B	30.77	1	30.77	415.17	< 0.0001	52.12	1	52.12	232.97	< 0.0001
C	94.09	1	94.09	1269.34	< 0.0001	48.87	1	48.87	218.40	< 0.0001
D	1.41	1	1.41	19.05	0.0006	3.101×10^{-3}	1	3.101×10^{-3}	0.014	0.9078
A ²	6.31	1	6.31	85.15	< 0.0001	0.017	1	0.017	0.076	0.7872
B ²	0.53	1	0.53	7.19	0.0171	10.45	1	10.45	46.71	< 0.0001
C ²	8.87	1	8.87	119.65	< 0.0001	0.029	1	0.029	0.13	0.7255
D ²	2.45	1	2.45	33.09	< 0.0001	0.026	1	0.026	0.12	0.7375
AB	0.19	1	0.19	2.60	0.1276	1.430×10^{-5}	1	1.430×10^{-5}	6.391×10^{-5}	0.9937
AC	0.24	1	0.24	3.26	0.0913	5.407×10^{-5}	1	5.407×10^{-5}	2.416×10^{-4}	0.9878
AD	0.016	1	0.016	0.22	0.6474	1.589×10^{-6}	1	1.589×10^{-6}	7.101×10^{-6}	0.9979
BC	1.64	1	1.64	22.16	0.0003	4.04	1	4.04	18.05	0.0007
BD	0.16	1	0.16	2.15	0.1633	8.163×10^{-4}	1	8.163×10^{-4}	3.649×10^{-3}	0.9526
CD	0.58	1	0.58	7.86	0.0134	1.965×10^{-3}	1	1.965×10^{-3}	8.782×10^{-3}	0.9266
Residual	1.11	15	0.074			3.36	15	0.22		
Lack of fit	1.07	10	0.11	12.62	0.0060	3.36	10	0.34	35643.63	< 0.0001
Pure error	0.042	5	8.47×10^{-3}			4.708×10^{-5}	5	9.416×10^{-6}		
Cor total	155.60	29				119.78	29			

A, pH; B, dose (m, g/L); C, DOX conc. (C_0 , mg/L); D, time (t , min)

Table 5 Various statistic *R*-squared values suggested by CCD for different responses

Responses	<i>R</i> -squared	Adj <i>R</i> -squared	Pred <i>R</i> -squared
% DOX removal (X_1)	0.99	0.98	0.96
Adsorption capacity (X_2)	0.97	0.94	0.83

positive associations towards both responses. It is shown in Table 5. Further assessment of the model adequacy has been investigated by plotting actual versus predicted values. Excellent correlation shown in Fig. 3 reveals the adequate relationship among the experimental and calculated values (Table 6).

Response surface analysis and optimization

The 3–D response surface plots found from the RSM/CCD model for two responses % DOX removal (X_1) and capacity (X_2) with different adsorption parameters, i.e., C (mg/L), m (g/L), t (min), and pH values, are shown in Fig. 4. These graphs illustrate the variations within different dependent and independent parameters which facilitate the analysis for single and simultaneous influence of the parameters on

studied responses. The corresponding values of both the responses with these parameters for DOX uptake are summarized in Table 2.

Figure 4a and d represent the interactive influence of C and m on the responses X_1 and X_2 , respectively. At any adsorbent dose, DOX uptake increases rapidly with enhancement in initial DOX concentration. This increment is continuous for high adsorbent dose but at low dose, % removal becomes ultimately constant at very high DOX concentrations. From Fig. 4d, it may be seen that increasing RHA dosage results in a decreasing adsorption capacity, whereas it increases with the DOX amount in solution. The maximum DOX removal was observed at the minimum RHA dosage and maximum DOX concentration. At constant RHA dose (5 g/L) and DOX concentration (90 mg/L), a maximum DOX uptake capacity of > 13 mg/g was obtained. Furthermore, the relations between DOX initial concentrations (mg/L) and time (min) were studied and are represented in Fig. 4b and e. As can be seen from Fig. 4b, % DOX removal enhanced rapidly with increment in its initial concentration till ≈ 80 mg/L, because of the larger amount of DOX competing for the available adsorption sites on RHA. Moreover, it was also noted that for very high initial concentrations, less adsorption time favors the DOX uptake, which might be ascribed to the desorption at more adsorption time. The interaction

Fig. 3 The actual data versus predicted data for removal (%) and capacity (mg/g) of DOX (**a**, **b**)

Table 6 Comparison of experimental and predicted responses values at optimized condition ($m=5$ g/L, $t=85.85$ min, $\text{pH}=6$, DOX concentration = 89.73 mg/L)

Responses	Predicted value	Experimental value
% removal (X_1)	99.51%	98.85%
Capacity (X_2)	16.25	17.74

between solution pH and initial concentration of DOX is exhibited in Fig. 4c and f. As it is evident from the figures, when initial DOX concentration increases, the removal rate of DOX by RHA increases significantly regardless of the changes in solution pH. In general, the influence of initial DOX concentration on DOX adsorption is greater than that of solution pH.

In DOX–RHA adsorption, optimization study was also performed for enhancing the performances X_1 and X_2 using the RSM. The optimization restrictions set for this purpose are given in Table S1. The conditions were evaluated as $m=5$ g/L, $t=85.85$ min and $\text{pH}=6$ with both responses as 99.51% and 16.25 mg/g, respectively. Further we examined the results of responses (percentage removal and capacity). These were 98.85% and 17.74 mg/g, respectively, which agree well with the advised values (Table 6).

Kinetics of DOX adsorption

To understand the kinetics of adsorption between DOX and RHA and calculate the kinetic parameters, pseudo-first-order- and pseudo-second-order kinetics models were used. It was performed under optimized conditions ($\text{pH}=6$, $m=5$ g/L, and time = 85.85 min) at different stock concentrations of DOX (40, 70, and 100 mg/L). These two model equations can be given by the following expressions:

Pseudo-1st-order model is represented as follows (Malik 2003):

$$q_t = q_e [1 - \exp(-k_f t)] \quad (7)$$

Pseudo-2nd-order model is signified as follows (Ho and McKay 1994):

$$q_t = \frac{tk_s q_e^2}{1 + tk_s q_e} \quad (8)$$

The initial adsorption rate, h (g/mg/min), may be calculated with the help of K_s and q_e magnitudes and are given as follows:

$$h = k_s q_e^2 \quad (9)$$

where q_e and q_t (mg/g) refer to the equilibrium amount of DOX adsorbed in duration t minutes, k_f (min^{-1}) and k_s

Fig. 4 3D-graph for the adsorptive removal of DOX from aqueous solution (a, b, c) % removal versus concentration of DOX, mass, time, and pH (d, e, f) capacity versus, DOX concentration, dose, t, and pH

Fig. 5 Pseudo-first and second-order adsorption kinetics at different initial concentrations (a) Weber–Morris plot versus t for DOX removal by RHA (b)

(g/mg/min) are the reaction constant rates for pseudo-1st and pseudo-2nd orders. As shown in Fig. 5a, initially, a sharp increase in sorption takes place due to the availability of high number of the active site on the adsorbent surface and equilibrium was attained within 30 min. The experimental data were correlated with these kinetic models with the help of nonlinear regression. It is evident from the figure that pseudo-2nd-order kinetic model fitted

better with the experimental values than pseudo-1st-order model. All the evaluated kinetic parameters, R^2 , and error values are listed in Table 7. High R^2 values and low MPSPD error at all concentrations (40, 70, and 100 mg/L) confirm that DOX sorption on the RHA follows the second-order kinetics.

In addition, the intra-particle diffusion (IPD) model was utilized to analyze the rate-controlling step in the DOX-RHA

Table 7 Kinetic model parameters for DOX adsorption on RHA at optimized parameters ($m = 5$ g/L, $t = 85.85$ min, and $\text{pH} = 6$)

	C_0 (mg L ⁻¹)		
	40	70	100
Pseudo-first-order			
k_f (min ⁻¹)	1.190	0.910	0.802
$q_{e,\text{exp}}$ (mg/g)	7.849	13.716	19.694
$q_{e,\text{cal}}$ (mg/g)	7.794	13.370	19.200
R^2 (non-linear)	0.988	0.992	0.990
MPSD	16.91	6.157	8.695
Pseudo-second-order			
k_s (g/mg/min)	0.580	0.360	0.276
h (mg/g/min)	35.771	67.042	102.622
$q_{e,\text{cal}}$ (mg/g)	7.853	13.644	19.287
R^2 (non-linear)	0.999	0.999	0.998
MPSD	0.928	3.790	7.315
Weber Morris			
k_{id1} (mg/g min ^{-1/2})	0.081	0.078	0.202
I_1	7.397	12.911	18.011
R^2	0.884	0.644	0.950
k_{id2} (mg/g min ^{-1/2})	0.001	0.012	0.026
I_2	7.822	13.546	19.282
R^2	0.326	0.481	0.451

adsorption process. The IPD model is represented by the following equation (Weber and Morris 1963):

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

where k_{id} (mg/g min^{1/2}) denotes the IPD rate constant and I (mg/g) is the intercept of the intraparticle diffusion plot, which also represents the width of boundary layer. In the Weber and Morris plot, if the q_t vs $t^{1/2}$ graph is linear and it crosses through the origin, it confirms that the sorption is controlled solely by internal diffusion. The process of the DOX sorption on surface can be confirmed in two steps by the Weber and Morris plot in Fig. 5b. The initial step represents the quick adsorption due to the higher number of active sites on the sorbent surface. This is denoted as intraparticle diffusion mechanism. The second part diminishes the intraparticle diffusion and attains the ultimate stability point as represented in the 2nd linear fragment in the figure. The second segment of the curves showed the equilibrium diffusion process. So, it can be said that the kinetic sorption process of DOX antibiotic onto RHA follows a multistep mechanism. The magnitude of IPD parameters k_{id} and I is listed in Table 7.

Isotherm modelling and thermodynamics

The adsorption of the DOX on RHA was examined at distinct temperatures and concentrations and the suitability of equilibrium data was evaluated with the various isotherm models as shown in Fig. 6. Freundlich (Freundlich 1906), Redlich-Peterson (R-P) (Redlich and Peterson 1959), and Langmuir isotherms (Langmuir 1918) are represented by the following equations.

Langmuir model:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (11)$$

Redlich-Peterson model:

$$q_e = \frac{K_{RC_e}}{1 + a_R C_e^\beta} \quad (12)$$

Freundlich model:

$$q_e = K_F C_e^{1/n} \quad (13)$$

where q_e (mg/g) is the specific equilibrium quantity of adsorbate, C_e (mg/L) is the equilibrium concentration of adsorbate, q_m (mg/g) is the maximum adsorption uptake. K_L , K_F , a_R , K_R are constants, and “ n ” represents the empirical constant.

The isotherm studies were performed at a temperature range of 288–318 K with DOX initial concentration of 40–300 mg/L. These experiments were directed at optimum conditions as $m = 5$ g/L, time = 85.85 min, and pH is 6. As displayed in Fig. 6, with the enhancement in temperature, the sorption rate increased due to the endothermic type of the operation. The non-linear fitting was performed and the experimental data suits well with the Langmuir, Freundlich, and R-P isotherm models with the high R^2 values. The values of parameters relevant to different isotherm models and correlation coefficient values are given in Table 8. The high R^2 values represent stronger interactions between adsorbate–adsorbent and as the value of β lies between 0 and 1 for R-P isotherm, it signifies that the sorption of DOX on RHA is a favorable operation.

The thermodynamic criterion is examined by Van't Hoff equation (Eq. (14)).

$$\ln K_d = \frac{-\Delta G^0}{RT} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R} \frac{1}{T} \quad (14)$$

where K_d is found from the slope of $\ln \frac{q_e}{C_e}$ versus q_e , T is the temperature in K, R represents the gas constant in J/mol/K, ΔG^0 , ΔH^0 , and ΔS^0 and are the changes in Gibb's free energy, standard enthalpy, and standard entropy.

Fig. 6 Equilibrium adsorption isotherms for DOX adsorption on RHA at optimized parameters ($m = 5$ g/L, $t = 85.85$ min, and $\text{pH} = 6$) **a** Langmuir isotherm model **b** Freundlich isotherm model **c** RP isotherm model. Experimental data points given by symbols and the lines predicted by isotherm model

Moreover, the evaluated thermodynamics parameters for DOX-RHA adsorption are listed in Table 8. The value of ΔH° was found as $6.226 \text{ kJ mol}^{-1}$. This positive value of ΔH° demonstrates that the sorption of DOX on RHA is an endothermic physical process. The evaluated values of ΔG° were $-ve$, and also, this value declines with the enhancement in temperature, which specifies adsorption is spontaneous, feasible, and also enhances with the heat addition. It is visible from the parameters that, as the temperature increases, ΔG° value increases, which indicates the enhancement in the sorption performance at higher temperatures. Moreover, the $+ve$ value of ΔS° approves the enhancement in the randomness of the DOX molecules at the solid–liquid interface in the adsorption process with the increment in the temperature (Lakshmi et al. 2009). So, from the thermodynamic investigation, it is concluded that adsorption of DOX on rice husk ash is spontaneous and endothermic process.

Mechanism of adsorption

The amphoteric quality of DOX permits the presence of several ionic species at distinct ranges of pH. The point of

zero charges of RHA was evaluated as 8.1. On the other hand, DOX shows three pK_a values ($\text{pK}_1 = 3.5$, $\text{pK}_2 = 7.7$, $\text{pK}_3 = 9.5$) (Gao et al. 2012). RHA has predominantly $+ve$ charge at $\text{pH} < \text{pHpzc}$ and $-ve$ charge when $\text{pH} > \text{pHpzc}$. At acidic pH, the interactions between the RHA and DOX are weak due to the presence of the same charges on both compounds. Under neutral conditions, the greater removal is obtained at that point because of the interactions between the RHA^+ and DOX° forms. At this pH, it shows that the H-bonding and electrostatic interactions are responsible for the adsorption of DOX by RHA as shown in Fig. 7. The RHA utilized for the present study was a heterogeneous fibrous and porous structure which composed mostly of silica. The $-\text{OH}$, $-\text{C}-\text{OH}$, $\text{Si}-\text{O}-\text{Si}$, and $\text{Si}-\text{H}$ groups present on the RHA surface played important role in adsorption of DOX. From FTIR, O_2 in the siloxane groups on the RHA and $-\text{OH}$ and amine groups of the doxycycline molecules are mainly responsible for the formation of H-bonding. On the other hand, the existence of electrostatic interactions is there amid the $-\text{OH}$ and ketone groups of the DOX and silanol groups present in the RHA.

Table 8 Isotherms and thermodynamics parameters for DOX adsorption on RHA at optimized parameters ($m = 5$ g/L, $t = 85.85$ min, and pH = 6)

ISOTHERMS						
Langmuir						
T (K)	K _L (L mg ⁻¹)	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	q _m (mg g ⁻¹)		R ²	CHI ²
288 K	0.036		73.631		0.999	0.137
303 K	0.019		128.934		0.997	0.321
318 K	0.022		130.116		0.997	0.131
Redlich-Peterson						
T (K)	K _R (L g ⁻¹)	$q_e = \frac{K_R C_e}{1 + a_R C_e^\beta}$	a _R (L mg ⁻¹) ^{1/β}	β	R ²	CHI ²
288 K	2.861		0.077	0.752	0.999	0.136
303 K	3.157		0.133	0.584	0.998	0.320
318 K	2.854		0.012	1.162	0.999	0.122
Freundlich						
T (K)	K _f (mg g ⁻¹)(mg L ⁻¹) ^{-1/n}	$Q_e = k_f C_e^{1/n}$	1/n		R ²	CHI ²
288 K	3.541		0.733		0.998	0.307
303 K	3.367		0.783		0.997	0.394
318 K	3.797		0.783		0.997	0.524
Freundlich						
T (K)	K × 10 ⁻³ (L kg ⁻¹)	$\ln K_D = \frac{-\Delta G^0}{RT} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R} \frac{1}{T}$	ΔG ₀ (kJ mol ⁻¹)		ΔH ₀ (kJ mol ⁻¹)	ΔS ₀ (J mol ⁻¹ K ⁻¹)
288 K	1.985		-18.182		6.226	84.519
303 K	2.069		-19.234			
318 K	2.544		-20.733			

Fig. 7 Adsorption mechanism for DOX on RHA surface

Solidification/stabilization performance and toxicity test

To ensure the safe disposal of exhausted adsorbent, it is necessary to capsule the antibiotic present in it to avoid its further mixing in the atmosphere. Results of solidification study are shown in Fig. 8, which shows that for all the studied concentrations (40, 70, and 100 mg/L), the encapsulation percentage was > 98%. The above results demonstrate that Portland cement can be used as a potential solidifying agent for almost complete encapsulation of antibiotics present in exhausted adsorbents.

The leachate was further tested to evaluate its toxicity for the possible presence of DOX into it. The comparative zone of inhibitions was observed on petri plates having EC and BC bacterial strains. From the results, it is evident that higher zones were found at 10 ppm (30 mm, 28 mm) and lower at 0.1 ppm for EC and 1 ppm for BC (11 mm, 14 mm) in both cases EC and BC (Fig. 9(a and b)). In Fig. 9c and d, there were no inhibition zones seen in the growth of EC and BC bacterial plates. Therefore, it is indicated that S/S process is a viable method for handling exhausted adsorbents as it could successfully capsule the antibiotic and no harmful effects against the selected bacterial strains were observed.

Fig. 8 % capsulation of DOX in cement for different adsorbent to cement mass ratios

Fig. 9 Zone of inhibition on *E.coli* (EC) and *Bacillus subtilis* (BC) bacterial strains, **a** for DOX samples on *E.coli* (EC) **b** for DOX samples on *Bacillus subtilis* (BC) **c** for leachate on *E.coli* **d** and *Bacillus subtilis*

Comparison of RHA with different sorbents

The adsorptive performance of RHA was compared with few earlier used sorbents for the uptake of DOX. Table 9 represents the DOX removal percentage for previously used sorbents in comparison with RHA from aqueous solution of DOX. Very high DOX removal in case of RHA as compared to others makes it an appropriate adsorbent for DOX removal. Application of RHA as an adsorbent for removal of pharmaceutical compounds may be helpful in solving the environmental issues and at the same time it will also reduce the load of RHA generated from incinerators.

Conclusion

In the present study, RHA was established as an effectual sorbent for the adsorption of doxycycline hydrochloride from its aqueous solution. It exhibited the strong sorption capacity by giving high values for both the responses, $X_1 = 98.85\%$ and $X_2 = 17.74 \text{ mg/g}$ at optimized parameters ($m = 5 \text{ g/L}$, $t = 85.85 \text{ min}$, DOX concentration = 89.73 mg/L , and $\text{pH} = 6$). From experimental kinetic results, pseudo-second-order model fitted better than pseudo-first-order. The positive and negative values of ΔH° and ΔG° respectively disclosed that the uptake of DOX on RHA surface

Table 9 Comparison of adsorptive performance of various adsorbents for DOX

Adsorbents	Maximum % DOX removal	References
Cobalt oxide	66.5	Abbas et al. 2019
PSSAC	85.82	Kaur et al. 2021c
Copper nitrate modified biochar (Cu-BC)	93.22	Liu et al. 2017
DES-PSSAC	96.30	Kaur et al. 2021b
Fe ₃ O ₄ magnetic nanoparticles	98.7	Ghaemi and Absalan 2015
Rice husk biochar	80.23	Zeng et al. 2018
chitosan composite	98.84	Rahman and Varshney 2021
RHA	98.85	This study

is endothermic and instantaneous type by nature. Lastly, the loaded RHA fixation via the S/S method while using Portland cement as a solidifying agent resulted as an effective and safe disposal technique. Cytotoxicity assessments showed that DOX leachate sample solutions are insufficient to get rid of the aquatic flora and fauna where whole life depends and we survive. This study suggests that RHA which is an agri-residue can be a very economical and effective adsorbent for treating the pharmaceutical wastes at industrial scale. This will minimize the bio waste load and accomplish the target of “treating waste by waste.”

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