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Optimization, equilibrium and kinetic studies on ibuprofen removal onto microwave assisted – activated *Aegle marmelos correa* fruit shell

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ABSTRACT

Micro pharmaceutical pollutant, ibuprofen, was removed from aqueous solutions by microwave irradiated thermally activated *Aegle marmelos correa* fruit shell (MTAS). The main and interactive effects of five process variables such as adsorbent dose (0.125–0.5 g L^{-1}), initial ibuprofen concentration (100–300 μg L^{-1}), contact time (1–3 h), pH (2–12) and temperature (20°C–40°C) were investigated via response surface methodology based on Box–Behnken statistical design. The optimum values of the key variables were estimated using Derringer's desirability function. The optimal values were found to be adsorbent dose 0.241 g, initial ibuprofen concentration 150 μg L^{-1}, pH 8.69, temperature 33.57°C and contact time 1.42 h with maximum desirability of 91%. The equilibrium data obeyed Redlich–Peterson isotherm which showed that the MTAS was heterogeneous and ibuprofen was adsorbed in multilayers. The kinetic investigation showed that the ibuprofen was chemisorbed on MTAS surface following Avrami's fractional-order kinetics. The thermodynamic parameters revealed that ibuprofen adsorption process was spontaneous and endothermic. Regeneration of exhausted MTAS found to be possible via acetic acid as eluent.

Keywords: Adsorption; Box–Behnken; Ibuprofen; *Aegle marmelos correa* fruit shell; Equilibrium

1. Introduction

The presence of pharmaceutical compounds in waste waters is becoming a major concern because they can have adverse effects on human health and on both terrestrial and aquatic ecosystems. Pharmaceutical compounds especially non-steroidal anti-inflammatory drugs are potentially critical due to their long-term exposure even at low concentration such as nano-level [1]. Whereas, commercially available well known anti-inflammatory drug ibuprofen is prescribed for the treatment of fever, migraine, muscle aches, arthritis and tooth aches. It is often sold over-the-counter due to its versatility and several metric tons of ibuprofen are synthesized worldwide every year [2]. Ibuprofen crosses the threshold

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limit of the environment through the pharmaceutical industrial effluents, human excrements and dumping of unused prescription drugs [1].

The conventional biological wastewater processing techniques are not efficient attributable to a significant persistence status that has been observed for ibuprofen [3]. Hence, new research efforts are now being made to find novel and efficient methods to be combined within the water treatment schemes. First line of activities include the conversion of ibuprofen into harmless compounds through photocatalysis [4], sonochemical degradation [5], chemical oxidation [6], ozonation [7], Fenton processes [3,8] and cavitation [9]. All these methods have been proposed only in recent times and, even if the outcomes are hopeful, there is still some ambiguity at the origin of degradation compounds and by-products, which should be further investigated. In order to overcome this downside and to work out an effective depuration technology, a second line of investigation discusses the application of adsorption process, largely conducted on either natural materials [10] or activated carbon [11,12].

Adsorption is an effective technique for desalination due to its cost effectiveness and versatility to use for wide variety of compounds [13–16]. Activated carbon, a widely used adsorbent had relatively high adsorption capacity for a wide variety of pollutants. Commercially available activated carbons are usually obtained from either wood or coal, and hence, are still considered expensive [17–20]. Because of this reason, the research has gained momentum towards preparation of adsorbents from agricultural by-products and waste materials [21–23]. Agricultural by-products or wastes are rich source of organic matter containing hydroxyl, carboxyl and amine groups which can easily enhance binding of cations [24,25].

This present study employs an interesting strategy choosing *Aegle marmelos correa* fruit shell as an abundantly available residue as well as precursor for the indigenous development of carbonaceous adsorbent that further permits to solve the problem associated with waste disposal and recycling. *Aegle marmelos correa* belongs to the family Rutaceae and is a tree growing up to 8.5 m height which is widely scattered all over the Indian peninsula along with Sri Lanka, Burma and Thailand [26,27]. In addition, the hard fruit shell from this tree is a readily available precursor which is unnoticed and obtainable in plenty. This cheap and renewable waste material can be utilized for adsorbent preparation.

The processing cost of adsorption-based effluent treatment is greatly minimized by optimum utilization of commercial activated carbons. The dynamic characteristic of adsorption process is very complex and hence obtaining the optimum process variables becomes vital to get the optimum pollutant removal efficiency. One of the methodologies for obtaining the optimum results is response surface methodology (RSM). The classical one variable at a time method is time consuming when large number of variables are considered. But RSM comprises the reduced number of experiments needed to examine the effect of variables and their interactions [28,29]. Therefore application of RSM in adsorption process modeling can result in better profit, reduced inconsistency and reduced development time and cost [24,26].

Keeping the above points in mind, an attempt was made to prepare a novel adsorbent from *Aegle marmelos correa* fruit shell for removing ibuprofen from aqueous solution. The influence of various operating variables and optimum process conditions for the ibuprofen adsorption were investigated using Box–Behnken statistical design (BBD), which is not tried till to the best of our knowledge. The experimental data were analyzed by isotherms, kinetics and thermodynamic parameters.

2. Material and methods

2.1. Preparation of ibuprofen solution

Ibuprofen was obtained from S.D. Fine-Chem Ltd., Mumbai. All other chemicals were obtained from Merck India Ltd., Mumbai. Stock solution of 1,000 μg L^{-1} of ibuprofen was prepared using deionized water. The working solutions were prepared from the stock solutions by diluting it to appropriate volumes. The initial solution pH was adjusted to the experimental conditions by the step wise addition of 0.1 N HCl or 0.1 N NaOH solutions before mixing the adsorbent with the ibuprofen solution. The concentration of ibuprofen in the sample was analyzed using a double beam UV–Vis spectrophotometer at its maximum wavelength.

2.2. Adsorbent preparation

Aegle marmelos correa fruits were obtained from local premises at Coimbatore, Tamil Nadu, India. The fruit shells were separated, and washed thoroughly with deionized water twice to remove impurities. Then the broken shells were crushed into pieces, ground to powder and sun dried (40°C ± 5°C) for 3 d. The bone dry shell powder was thermally activated in microwave oven at 600 W for 15 min. Finally, the blackish material obtained, microwave-assisted thermally activated *Aegle marmelos correa* fruit shell (MTAS), was sieved and kept in an airtight container for further batch experiments.

2.3. Characterizations of MTAS

The iodine number and methylene blue number of MTAS was calculated based on the ASTM 4607–86 standards at 298 K. The specific surface area of MTAS was measured using a surface analyzer (Micromeritics ASAP 2020). Surface morphology was examined by using a scanning electron microscope (SEM: JSM–6390LV, JEOL Ltd., Japan). The functional groups present on the MTAS surface were determined using Boehm titrations.

2.4. Batch adsorption

Batch adsorption experiments were conducted according to BBD. The adsorbent–ibuprofen solution mixtures were taken in a 250 mL Erlenmeyer flasks and agitated in a thermo-regulated shaker (GeNei SLM–IN–OS–16, India) operating at 180 rpm. The samples were withdrawn from the flasks at predetermined time intervals. The collected samples were centrifuged at 10,000 rpm and the supernatant was analyzed by using double beam UV–Vis spectrophotometer (ELICO, India) at 220 nm. Experimental analysis was repeated three times and the results were statistically analyzed. Percentage

of ibuprofen removal from bulk ibuprofen solution was calculated using the following equation:

$$\%R = \frac{C_i - C_0}{C_i} \times 100 \quad (1)$$

where C_i and C_0 (μg L^{-1}) are initial and final concentration of the ibuprofen in the aqueous solution. The ibuprofen adsorption capacity q_t (μg g^{-1}) at any time t was determined as:

$$q_t = \left(C_i - C_t\right) \times \frac{V}{M} \quad (2)$$

where C_t (μg L^{-1}) is concentration of ibuprofen at any time t, V (L) is volume of ibuprofen solution and M (g) is amount of MTAS.

2.5. Box–Behnken design

The BBD, a widely used RSM, is a spherical, revolving design and a second-order multivariate technique based on three-level fractional factorial design consisting of a full 2^2 factorial scattered into a balanced incomplete block design [24,26]. BBD was chosen to study the effects of pH, temperature, adsorbent dosage, initial concentration and contact time on ibuprofen adsorption. The experimental design was given in Table 1. A second-order polynomial equation correlating the effect of variables in terms of linear, quadratic and cross product terms was employed to predict the percentage removal of ibuprofen. The general equation is of the form:

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{j=1}^{k} \beta_{ji} X_i^2 + \sum_{i=1}^{k} \sum_{j<i=1}^{k} \beta_{ji} X_i X_j + \epsilon \quad (3)$$

where Y is the response; k is the number of the patterns; i and j are the index numbers for pattern; β_0 is the free or offset term called intercept term; X_1, X_2… X_k are the coded independent variables; β_i is the first-order (linear) main effect; β_{ii} is the quadratic (squared) effect; β_{ij} is the interaction effect and ε is the random error which allows for discrepancies or uncertainties between predicted and measured values.

Table 1
Characteristics of MTAS

Parameter	Before adsorption	After adsorption
BET surface area	887 m^2 g^{-1}	4 m^2 g^{-1}
Total pore volume	0.587 cm^3 g^{-1}	0.107 cm^3 g^{-1}
Micropore volume	0.255 cm^3 g^{-1}	0.102 cm^3 g^{-1}
Mesopore volume	0.132 cm^3 g^{-1}	0.005 cm^3 g^{-1}
Carboxylic groups	2.65 mmol g^{-1}	2.61 mmol g^{-1}
Lactonic groups	0.56 mmol g^{-1}	0.50 mmol g^{-1}
Phenolic groups	1.12 mmol g^{-1}	1.01 mmol g^{-1}
Carbonyl groups	0.34 mmol g^{-1}	0.29 mmol g^{-1}

2.6. Statistical analysis

Experimental design data were analyzed using multiple regressions through the least square method. The significance of the regression coefficients was tested by F-test. It was also used to verify the statistical significance of models at $p = 0.05$ using the Statistical Software Design Expert 8.0.7.1 (Stat-Ease Minneapolis, USA). The results were analyzed using the Pareto analysis of variance (ANOVA) and ANOVA tables were generated. The quality of fit of the polynomial equation was expressed with the coefficient of determination (R^2). The effect and regression coefficients of linear, quadratic and interaction terms were determined. Models and response surfaces were generated for each response.

2.7. Isotherms and kinetics

The batch equilibrium data obtained for five different initial concentrations (100, 150, 200, 250 and 300 μg l^{-1}) at pH 12, temperature 313 K and contact time 180 min was fitted to isotherms such as Langmuir [30], Freundlich [31] and Redlich–Peterson [32]. Batch experiments were carried out for differential concentrations (100, 150, 200, 250 and 300 μg L^{-1}) at pH 12, temperature 313 K and contact time 180 min to investigate the adsorption kinetics. Kinetic equations including Ho [33] and Avrami [34] were employed for testing the batch kinetic data.

The isotherm and kinetic parameters were determined using MATLAB® non-linear curve fitting tool. The statistical parameters such correlation coefficient (R^2) and root mean square error (RMSE) were considered for examining the correlations. The R^2 close to unity and smaller RMSE is the index to select the suitable correlation [18,24,26].

2.8. Thermodynamics

Batch experiments were carried out for differential temperatures (293, 303, 313 and 323 K) at pH 12, initial concentration 150 μg L^{-1} and contact time 180 min to examine the adsorption thermodynamics. The thermodynamic parameters were calculated from the following equations [35,36]:

$$\ln\left(\frac{q_e}{C_e}\right) = \frac{\Delta S^0}{2.303R} - \frac{\Delta H^0}{2.303RT} \quad (4)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (5)$$

$$\Delta H_{is} = \frac{d\left(\ln C_e\right)}{d(1/T)} \quad (6)$$

where R is gas constant (8.314 J mol^{-1} K^{-1}) and T is the absolute temperature (K).

3. Results and discussions

3.1. Characterizations of MTAS

The amount of micropores (<2.0 nm) developed on the adsorbent surface is estimated using iodine number, whereas the development of mesopores (2–50 nm)

is calculated via methylene blue number [37]. The iodine number and methylene blue number of MTAS were measured to be 672 mg g^{-1} and 54 mg g^{-1}, respectively. Fig. 1 shows the comparison of ibuprofen adsorption onto MTAS and raw bilva shell powder. It is inferred that microwave irradiation aided increase in surface area which helped MTAS to adsorb ibuprofen higher than raw shell powder. Comparison of SEM micrographs (Fig. 2) also revealed the formation of good number of pores. The BET surface area was found to be 887 m^2 g^{-1}. This conferred the excellent development of pores on its surface. Boehm titration provides evidence for the existence of surface functional groups such as carboxylic, lactonic, phenolic and carbonyl contributing to surface acidity [38]. The comparison of surface area and pore volume values before and after ibuprofen adsorption is presented in Table 1. The diminution in surface area and pore volume values indicated that ibuprofen is adsorbed physically [39]. The strength of each functional group determined via Boehm titrations before and after ibuprofen adsorption showed that a negligible amount of surface functional groups took part in the adsorption process. It is the indication that the adsorption may be favored by electrostatic attraction [40]. The variations in FTIR spectra of MTAS before and after adsorption (Fig. 3) are insignificant which indicated that pore diffusion is the major part of adsorption process [41].

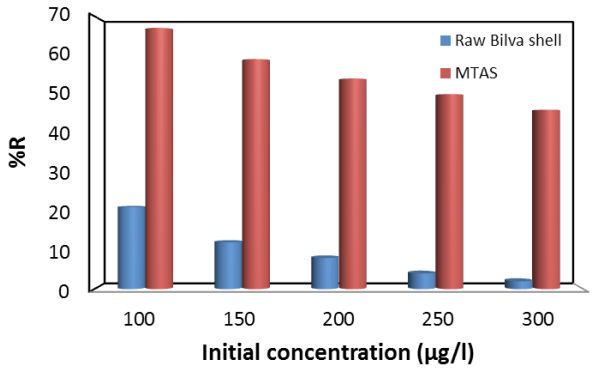

Fig. 1. Comparison of ibuprofen adsorption onto raw bilva shell and MTAS.

3.2. Box–Behnken design

Experiments were carried out according to the BBD matrix, in order to study the combined effects of the selected variables on percentage ibuprofen removal. Table 2 displays the BBD matrix, experimental and predicted percentage ibuprofen removal values. Linear, interactive, quadratic and cubic models were fitted to the experimental data to obtain the regression models. To decide about the adequacy of models among various models to percentage ibuprofen removal, two different tests namely the sequential model sum of squares and model summary statistics were carried out and the results are given in Tables 3(a) and 3(b), respectively.

The fit summary of the output indicates that the quadratic model is statistically highly significant and the p value was lower than 0.0001. This means that at least one of the terms in the regression model has a significant

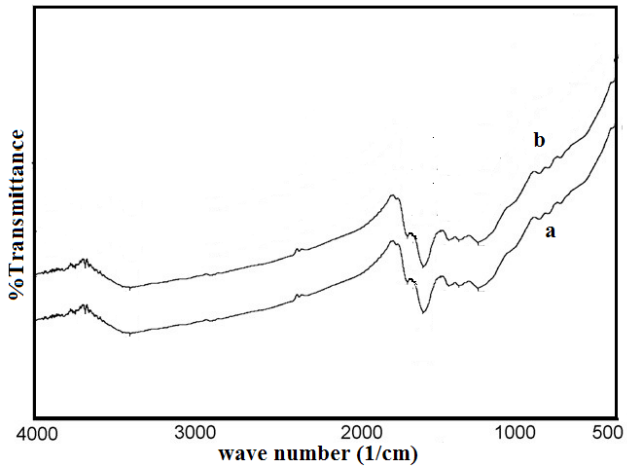

Fig. 3. FTIR spectra of MTAS before (a) and after (b) activation.

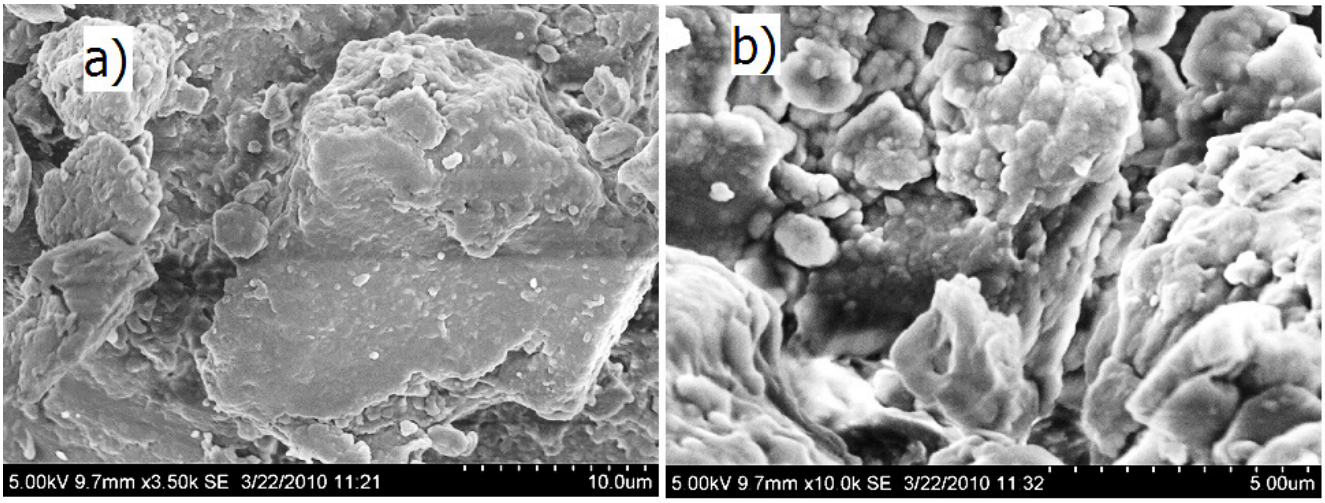

Fig. 2. SEM micrographs of MTAS before (a) and after (b) activation.

Table 2
BBD design matrix with actual and predicted values

S.no	A Dosage (g L^{-1})	B Concentration (μg L^{-1})	C Time (h)	D pH	E Temperature (°C)	$\%R_{act}$	$\%R_{pre}$
1	–1(0.625)	–1(50)	0(2)	0(7)	0(30)	58.12	57.83
2	1(2.5)	–1(50)	0(2)	0(7)	0(30)	57.91	57.71
3	–1(0.625)	1(150)	0(2)	0(7)	0(30)	47.85	47.85
4	1(2.5)	1(150)	0(2)	0(7)	0(30)	60.87	60.97
5	0(1.56)	0(100)	–1(1)	–1(2)	0(30)	41.57	41.43
6	0(1.56)	0(100)	1(3)	–1(2)	0(30)	43.35	43.29
7	0(1.56)	0(100)	–1(1)	1(12)	0(30)	50.78	50.71
8	0(1.56)	0(100)	1(3)	1(12)	0(30)	51.01	51.01
9	0(1.56)	–1(50)	0(2)	0(7)	–1(20)	56.12	56.55
10	0(1.56)	1(150)	0(2)	0(7)	–1(20)	53.41	53.79
11	0(1.56)	–1(50)	0(2)	0(7)	1(40)	68.57	68.29
12	0(1.56)	1(150)	0(2)	0(7)	1(40)	64.64	64.33
13	–1(0.625)	0(100)	–1(1)	0(7)	0(30)	37.35	37.54
14	1(2.5)	0(100)	–1(1)	0(7)	0(30)	46.82	46.66
15	–1(0.625)	0(100)	1(3)	0(7)	0(30)	40.9	41.24
16	1(2.5)	0(100)	1(3)	0(7)	0(30)	45.12	45.12
17	0(1.56)	0(100)	0(2)	–1(2)	–1(20)	40.54	40.23
18	0(1.56)	0(100)	0(2)	1(12)	–1(20)	44.13	44.31
19	0(1.56)	0(100)	0(2)	–1(2)	1(40)	47.13	46.95
20	0(1.56)	0(100)	0(2)	1(12)	1(40)	59.57	59.87
21	0(1.56)	–1(50)	–1(1)	0(7)	0(30)	63.65	63.76
22	0(1.56)	1(150)	–1(1)	0(7)	0(30)	54.31	54.18
23	0(1.56)	–1(50)	1(3)	0(7)	0(30)	58.47	58.62
24	0(1.56)	1(150)	1(3)	0(7)	0(30)	61.57	61.48
25	–1(0.625)	0(100)	0(2)	–1(2)	0(30)	35.92	35.97
26	1(2.5)	0(100)	0(2)	–1(2)	0(30)	41.75	41.91
27	–1(6.25)	0(100)	0(2)	1(12)	0(30)	44.05	43.91
28	1(2.5)	0(100)	0(2)	1(12)	0(30)	50.98	50.97
29	0(15.63)	0(100)	–1(1)	0(7)	–1(20)	41.15	41.15
30	0(15.63)	0(100)	1(3)	0(7)	–1(20)	42.51	42.28
31	0(15.63)	0(100)	–1(1)	0(7)	1(40)	52.2	52.34
32	0(15.63)	0(100)	1(3)	0(7)	1(40)	53.47	53.37
33	–1(0.625)	0(100)	0(2)	0(7)	–1(20)	35.47	35.2
34	1(2.5)	0(100)	0(2)	0(7)	–1(20)	41.58	41.4
35	–1(0.625)	0(100)	0(2)	0(7)	1(40)	45.91	46.04
36	1(2.5)	0(100)	0(2)	0(7)	1(40)	52.61	52.84
37	0(1.56)	–1(50)	0(2)	–1(2)	0(30)	58.02	58.29
38	0(1.56)	1(150)	0(2)	–1(2)	0(30)	53.11	53.33
39	0(1.56)	–1(50)	0(2)	1(12)	0(30)	65.31	65.19
40	0(1.56)	1(150)	0(2)	1(12)	0(30)	63.61	63.43
41	0(1.56)	0(100)	0(2)	0(7)	0(30)	65.01	65.02
42	0(1.56)	0(100)	0(2)	0(7)	0(30)	64.98	65.02
43	0(1.56)	0(100)	0(2)	0(7)	0(30)	65.02	65.02
44	0(1.56)	0(100)	0(2)	0(7)	0(30)	65.01	65.02
45	0(1.56)	0(100)	0(2)	0(7)	0(30)	65.03	65.02
46	0(1.56)	0(100)	0(2)	0(7)	0(30)	65.05	65.02

correlation with percentage ibuprofen removal. Cubic model was found to be aliased. Model summary statistics showed that the excluding cubic model which was aliased, quadratic model was found to have maximum adjusted R^2 and predicted R^2 values. Therefore, quadratic model was chosen for further analysis.

Table 3(a)
Adequacy of models tested for adsorption of ibuprofen onto MTAS

Source	R^2	R^2_{adj}	R^2_{pre}	PRESS	F-value	*p* value Probability > F	Remarks
Linear	0.2410	0.1461	0.0298	4,048.21	1,65,529.62	<0.0001	
2FI	0.2680	–0.0980	–0.6363	6,827.90	2,23,483.55	<0.0001	
Quadratic	0.9996	0.9993	0.9984	6.50	148.43	<0.0001	Suggested
Cubic	1.0000	0.9999	0.9981	7.77	44.42	0.0004	Aliased

Table 3(b)
ANOVA and statistical values for batch adsorption of ibuprofen onto MTAS

Source	Coefficient estimate	Standard error	F-value	*p* value Probability > F
Model	65.02	0.10	3,207.27	<0.0001
A	3.25	0.06	2,606.01	<0.0001
B	–1.68	0.06	690.35	<0.0001
C	0.54	0.06	70.59	<0.0001
D	4.25	0.06	4,450.99	<0.0001
E	5.57	0.06	7,645.98	<0.0001
AB	3.31	0.13	672.95	<0.0001
AC	–1.31	0.13	105.97	<0.0001
AD	0.28	0.13	4.65	0.0408
AE	0.15	0.13	1.34	0.2583
BC	3.11	0.13	594.98	<0.0001
BD	0.80	0.13	39.62	<0.0001
BE	–0.31	0.13	5.72	0.0246
CD	–0.39	0.13	9.24	0.0055
CE	–0.02	0.13	0.03	0.8613
DE	2.21	0.13	301.13	<0.0001
A^2	–12.90	0.09	22,318.04	<0.0001
B^2	3.97	0.09	2,110.68	<0.0001
C^2	–9.48	0.09	12,053.96	<0.0001
D^2	–8.93	0.09	10,695.43	<0.0001
E^2	–8.25	0.09	9,124.36	<0.0001
Lack of fit	–	–	14.84	0.0051
C.V%	0.48			
Adequate precision	192.09			

3.3. Model fitting and its adequacy

A quadratic model expressed by a second-order polynomial equation with interaction terms was fitted between the experimental values obtained on the basis of BBD [42,26,29]. The final equation obtained in terms of coded factors is given below:

$$\begin{aligned}\%R = {} & +65.02 + 3.25A - 1.68B + 0.54C + 4.25D + 5.57E \\ & + 3.31AB - 1.31AC + 0.28AD + 0.15AE + 3.11BC \\ & + 0.80BD - 0.30BE - 0.39CD - 0.022CE + 2.21DE \\ & - 12.90A^2 + 3.97B^2 - 9.48C^2 - 8.93D^2 - 8.25E^2\end{aligned} \quad (7)$$

Pareto ANOVA was used to analyze the experimental data and the results are listed in Table 3(b). The higher model F-value (3,207.27) and the associated lower *p* value ($p < 0.0001$) demonstrated the significance of the developed models and also indicated that most of the variation in the responses could be explained by the developed regression equation [43,26,29]. The high value of R^2 (0.9996), R_{adj}^2 (0.9993) and R_{pre}^2 (0.9984) demonstrated that, the form of the model chosen to represent the actual relationship between the percentage ibuprofen removal and selected variables is well correlated and accurate. Low value of coefficient of variance (0.48) displayed the high degree of precision and good reliability of the conducted experiments [42,26,29]. In this study, the adequate precision (signal-to-noise ratio) was found to be 192.09 (greater than 4), which indicates the best fitness of the developed quadratic second-order polynomial model.

Data were also analyzed to check the normality of the residuals. Normal probability plots of the residuals are shown in Fig. 4(a). The data points on this plot lie reasonably close to a straight line and show that the developed model is accurate. The parity plot which relates actual and predicted value is shown in Fig. 4(b). The straight line fit of this plot also indicates the adequacy of developed model to navigate the design surface.

3.4. Response surface analysis

Three-dimensional (3D) response surface plots and their corresponding contour plots are more helpful in understanding both the main and the interaction effects of the variables on the responses [26,29]. Therefore, 3D response surface plots (Figs. 5(a)–(i)) for percentage ibuprofen removal were formed based on the quadratic polynomial model developed (Eq. (7)). Since the regression model has five independent variables, three factors were held constant at the center level for each plot, hence, a total of 10 response 3D plots and 10 corresponding contour plots were produced. The nonlinear nature of all 3D response surfaces and the respective contour plots demonstrated that there were reasonable

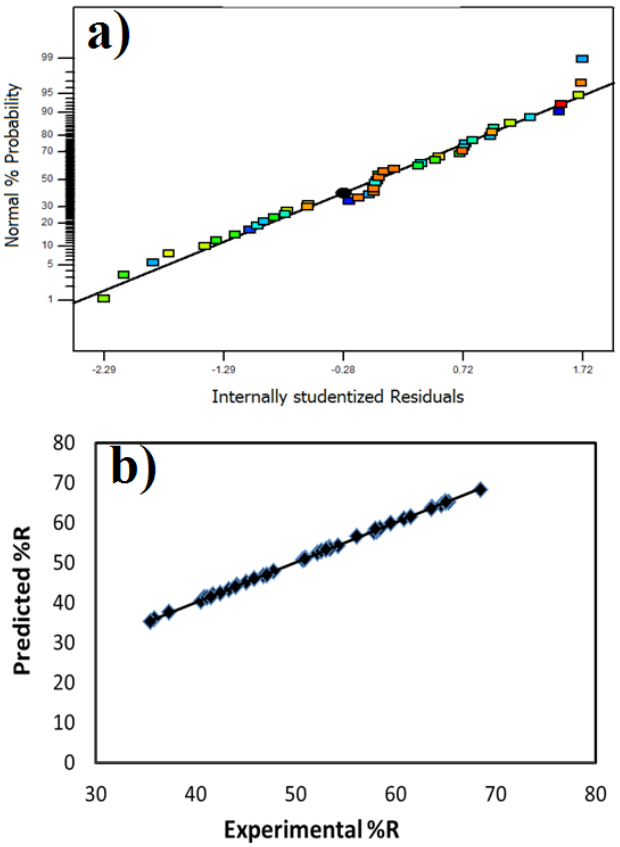

Fig. 4. (a) Normal probability plot and (b) parity plot.

interactions between each of the independent factors and the percentage ibuprofen removal. The individual effects of process factors on percentage ibuprofen removal were discussed below:

The combined effects of temperature with other variables were shown in Figs. 5(d), (g), (i) and (j), respectively. The temperature displayed a positive linear and quadratic effect on the percentage ibuprofen removal (Table 3(b)). When the temperature increased from 20°C to 40°C, the percentage ibuprofen removal was increased which indicated that the ibuprofen adsorption were favorable at elevated temperatures. This was owing to the increased surface activity and kinetic energy of the ibuprofen molecules [12].

Figs. 5(c), (f), (h) and (j) illustrate the effects of pH on percentage ibuprofen removal while keeping other three factors at center level. At larger pH, the negative charge density on the MTAS surface increased due to the reduction of hydrogen ions concentration on the sorption sites and that enabled the electrostatic attraction of the ibuprofen cations. But at low pH, the competition between hydrogen and ibuprofen ions on the sorption sites led to the high density of hydrogen ions which did not favor the ibuprofen adsorption. Similar results were also reported in literatures for different biomass systems [44].

The combined effects of MTAS dosage correspond with initial concentration, MTAS dosage, pH and temperature are shown in Figs. 5(a), (e), (f) and (g), respectively. From the figures, it can be seen that the dosage had positive effect on the percentage removal while its value increased from low (1.25 g L^{-1}) to high (5 g L^{-1}). An increase in dosage of MTAS increased the surface area and therefore more availability of active sites to ibuprofen molecules that caused an improvement in ibuprofen removal [44].

The combined effects of initial ibuprofen concentration on percentage ibuprofen removal are denoted by Figs. 5(a), (e), (h) and (i) response surface plots. The percentage of ibuprofen removal decreased with an increase in initial concentration. The unavailability of active sites to ibuprofen molecules on MTAS particles due to higher concentrations was the reason for it [45].

The 3D response surface plots such as Figs. 5(b), (e), (h) and (i) depicted the combined effects of contact time with other variables. Increase in percentage removal noted while contact time increased but there was sluggishness in the ibuprofen adsorption after a short period of time (<30 min) owing to the macropore diffusion followed by micropore diffusion [44,45].

3.5. Optimization using Derringer's desirability function

The Derringer's desirability function method [46] was employed to optimize the process variables. This desirability function searches for a combination of variable levels that mutually optimize a set of responses by satisfying the requirements for each response in the design [24,26]. By seeking from 29 starting points in the response surface changes, the best local maximum was found to be at adsorbent dose: 0.241 g, initial ibuprofen concentration: 150 μg L^{-1}, pH: 8.69, temperature: 33.57°C and contact time: 1.42 h, with maximum desirability of 91%. Confirmatory experiments were conducted using the optimized variables and the obtained percentage ibuprofen removal (59.11%) were closely related with the data (59.26%) obtained from optimization analysis. This indicates BBD combined with Derringer's desirability function could be effectively used to optimize the batch adsorption process variables for the percentage removal of ibuprofen.

3.6. Isotherms and kinetics

The equilibrium data analysis values are presented in Table 4. Redlich and Peterson equation includes the characteristics of both Langmuir and Freundlich isotherms into a single equation to represent adsorption equilibrium over a wide range of concentrations. The Redlich–Peterson model exponent (β_{RP}) value tends to zero when this isotherm approaches Freundlich isotherm and tends to unity while this isotherm approaches Langmuir isotherm. By comparing statistical parameters, Langmuir and Freundlich isotherms seemed to fit the equilibrium data poorly. The low values of RMSE (1.088) and high value of R^2 (0.996) indicated that Redlich–Peterson isotherm properly correlated the equilibrium data. This implied that the MTAS was heterogeneous in the liquid phase and ibuprofen removal was a multilayer adsorption process. The near unity value of β_{RP} (0.857) is also confirmed by this fact. The data presented in Table 4 compares the different types of isotherms used for the removal of ibuprofen.

In order to investigate the specific rate constant of the present adsorption reactions, the kinetic data have

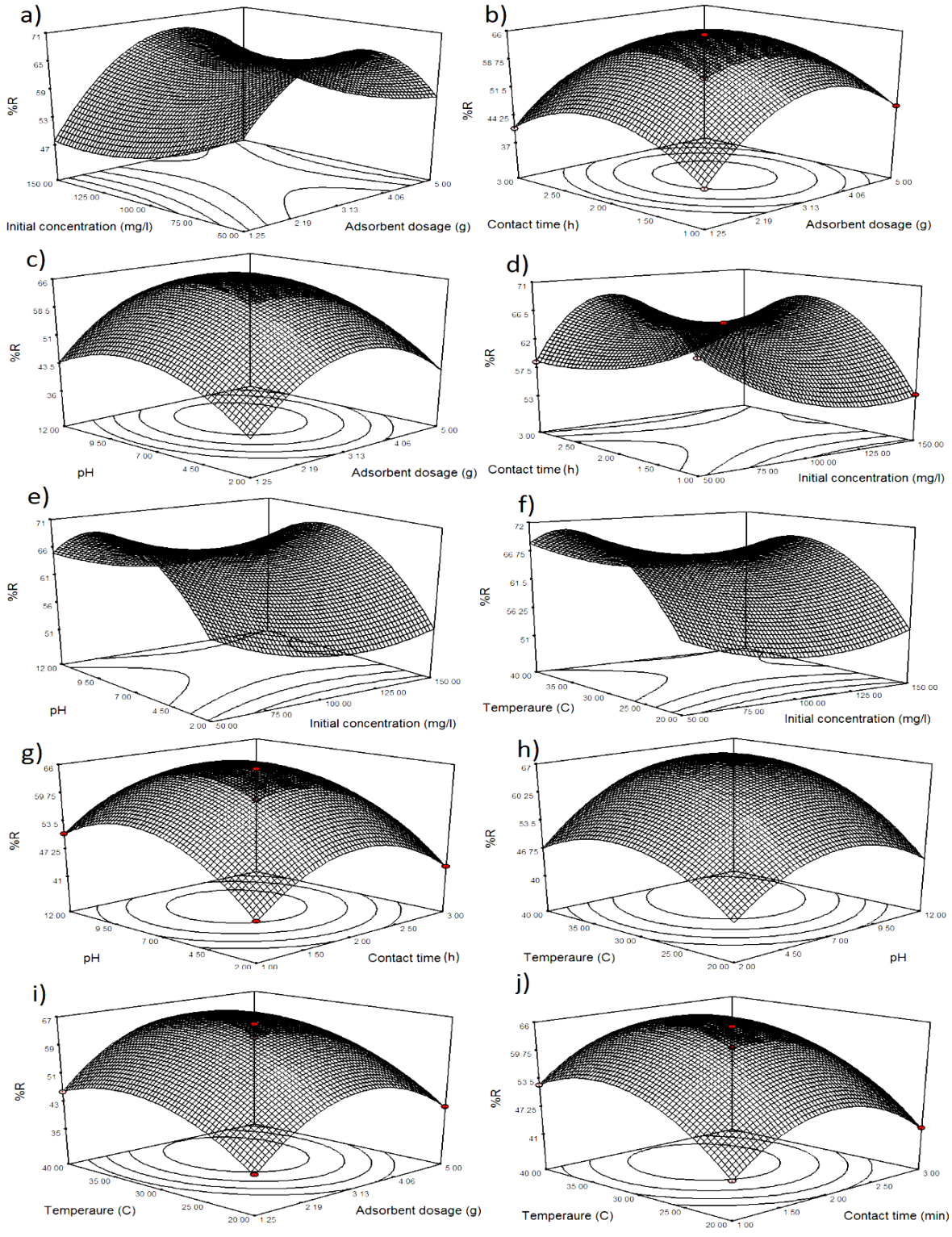

Fig. 5. 3D response surfaces and contour plots of ibuprofen–MTAS batch adsorption system.

been analyzed by Ho and Avrami kinetic models and the calculated parameters are presented in Table 5. While comparing the selected models, the higher values of R^2 and smaller values of RMSE over the selected concentration range shows that Avrami model correlated the kinetic data better than Ho model. It is also seen from Table 5 that when the concentration increased, the rate constant (K_A) values subsequently decreased and the uptake capacity ($q_{e,A}$)

increased. Further, the fractional order (n_A) and rate constant (K_A) values are almost similar for every concentration in both the ibuprofens. This meant that the higher concentration favored the uptake of both the ibuprofen but led unavailability of active sites to the ibuprofen molecules [33].

3.7. Thermodynamics

Variations of standard thermodynamic parameters during the adsorption process were evaluated and are presented in Table 6. As seen, the adsorption of ibuprofen by MTAS was spontaneous with the negative values of ΔG^0 [47]. The value of ΔH^0 was positive which described that the ibuprofen adsorption was endothermic in nature [30]. The positive ΔS^0 indicated that there are some structural changes in the MTAS particles as well as ibuprofen during the adsorption process [23].

Table 4
Isotherm parameters

S.no	Isotherm	Parameters	Values
1	Langmuir	Q_{mL} (μg g^{-1})	50.310
	$q_e = \frac{q_{mL} b_L C_e}{1 + b_L C_e}$	b_L (L μg^{-1})	0.126
		R_L	0.033
		R^2	0.991
		RMSE	1.780
2	Freundlich	K_F (L g^{-1})	8.688
	$q_e = K_F C_e^{1/n_F}$	n_F	2.231
		R^2	0.970
		RMSE	3.199
3	Redlich–Peterson	K_{RP1} (L g^{-1})	7.871
	$q_e = \frac{K_{RP1} C_e}{1 + K_{RP2} C_e^{\beta_{RP}}}$	K_{RP2} (L μg^{-1})	0.271
		β_{RP}	0.857
		R^2	0.996
		RMSE	1.088

3.8. Regeneration

The production charge for MTAS is only based on the microwave irradiation as *Aegle marmelos correa* fruit shells are cheaply available. The cost of MTAS can be further reduced if it could be regenerated for further use. It was found from laboratory experiments that MTAS could be regenerated efficiently using hot water (80°C ± 2°C). From Fig. 6, it is seen that hot water regenerated the MTAS more than eight times for further usage. This fact also supported that *Aegle marmelos correa* fruit shell could be a cost-effective adsorbent for ibuprofen bearing effluents.

4. Conclusions

Microwave-assisted activated waste *Aegle marmelos correa* fruit shell was utilized as adsorbent for the batch adsorption of ibuprofen. The main and interactive effects of five process variables such as adsorbent dose, initial ibuprofen concentration, contact time, pH and temperature were investigated using Box–Behnken statistical design. The simultaneous optimization by Derringer's desirability function indicated that 59.26% removal of ibuprofen could be possible at the optimal conditions. Isotherm studies indicated that ibuprofen adsorption on to MTAS was a multilayer adsorption. The kinetic

Table 6
Thermodynamic parameters for ibuprofen adsorption onto MTAS

T (K)	ΔG^0 (kJ mol^{-1})	ΔH^0 (J mol^{-1})	ΔS^0 (J mol^{-1} K^{-1})
293	–45.21	678.04	156.64
303	–46.78		
313	–48.34		
323	–49.91		

Table 5
Kinetic parameters at various ibuprofen concentrations

Model	Parameter	100 (μg L^{-1})	150 (μg L^{-1})	200 (μg L^{-1})	250 (μg L^{-1})	300 (μg L^{-1})
Ho	K_{Ho} (g μg^{-1} min^{-1})	0.011	0.004	0.002	0.002	0.001
$q_t = \frac{q_{e,Ho}^2 k_{Ho} t}{1 + k_{Ho} q_e t}$	$Q_{e,Ho}$ (μg g^{-1})	10.799	20.671	31.108	40.710	49.557
	h	1.297	1.868	2.349	2.582	2.856
	R^2	0.963	0.990	0.975	0.963	0.955
	RMSE	1.322	1.292	3.075	4.911	6.595
Avrami	K_A (min^{-1})	0.287	0.269	0.252	1.000	0.235
$q_t = q_{e,A}\left[1 + \exp\left(-k_A t\right)^{n_A}\right]$	n_A	0.287	0.269	0.252	0.240	0.235
	$Q_{e,A}$ (μg g^{-1})	9.808	18.246	27.187	35.043	42.185
	R^2	0.981	0.993	0.992	0.984	0.982
	RMSE	0.932	1.064	1.733	3.226	4.118

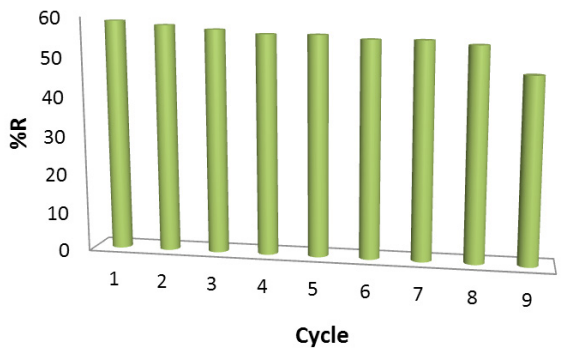

Fig. 6. Regeneration capacity of MTAS.

investigation showed that the ibuprofen adsorption on MTAS surface follows Avrami's fractional-order kinetics. The thermodynamic studies revealed that adsorption process was spontaneous and endothermic. Regeneration studies revealed that MTAS could be regenerated more than eight times for further usage.

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