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Modified phyto-waste *Terminalia catappa* fruit shell: A reusable adsorbent for the removal of micropollutant diclofenac

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Abstract

This study investigated the preparation of reusable adsorbent from phyto-waste *Terminalia catappa* fruit shell by acid-thermal modification and utilization for the removal of diclofenac from the aqueous system. The structural characteristic features of the modified *T. catalpa* fruit shell (MTCFS) was analysed using Scanning Electron Microscopy, Fourier Transform Infrared Spectroscopy and Brunauer-Emmett-Teller. Batch experiments proved that temperature and pH are mainly influenced the adsorption process. Langmuir and Freundlich isotherms were obeyed for the diclofenac adsorption. Temkin isotherm model revealed that increasing temperature affected the adsorption of diclofenac. Dubinin Radushkewick isotherm indicates that the present adsorption system achieved through physical interaction. Pseudo-second-order kinetic model was well fitted for the diclofenac adsorption. Intraparticle diffusion results show that increasing in the rate of adsorption and increase in the boundary layer thickness. The thermodynamic results revealed that increasing the temperature inversely affected the diclofenac adsorption. Recycling experiments confirmed that the MTCFS was found to be quite stable and retained its adsorption efficiency up to eight cycles for diclofenac removal.

Keywords**:** *Terminalia catappa*, acid-thermal modification, removal, diclofenac, kinetics, isotherm models, thermodynamics, reusability

1 Introduction

Diclofenac (2-[(2,6-dichlorophenyl) amino] benzeneacetic acid) is a synthetic non-steroidal anti-inflammatory drug, widely used in human and veterinary medicine.[1] It has been reported that the residual subsistence of diclofenac in various water bodies was found up to μg L^{-1}, which might cause threats to living beings.[2-4] The toxicity of diclofenac and their metabolism to human being have been studied extensively.[2] Recently, Chae *et al*.[5] determined that diclofenac is a developmental toxicant and teratogen in Xenopus embryos. Sathishkumar *et al*.[6] observed the cytotoxicity of diclofenac on mouse fibroblast 3T3-L1 preadipocytes. The formation of more toxic mid-byproducts of diclofenac during the disinfection process poses a potential risk to consumers.[7] Furthermore, the biomagnifications of diclofenac in food chain lead to the unpredictable negative effects on non-target ecological species.[8] Therefore, the removal of diclofenac in water sources assumes very essential before biomagnification through food chain. In order to solve this environmental issue, researchers have been trying to develop various innovative techniques for the removal of diclofenac.

Different kind of physico-chemical and biological methods have been proposed for the diclofenac removal including molecularly imprinted polymer microspheres,[9] granular activated carbon filtration,[10,11] bagasse,[12] ultrasonic irradiation,[13] pulsed corona discharge,[14] enzymatic biotransformation,[6,15] electron beam irradiation combined with a biological aerated filter[16] and combined processes based on hydrodynamic cavitation and heterogeneous photocatalysis.[17] However, the implementation of these techniques is still not feasible or only partially efficient for the field applications due to the high costs, low selectivity, limited performance in the competitive removal of interfering organic matters and also may be generated toxicologically relevant oxidation by-products during the treatment processes. Thus, a promising alternative for

the wastewater treatment that contain pharmaceutical active compounds (PhACs) concerns the adsorption processes that utilize phyto-waste derived materials as adsorbents.[18]

In the point of environmental consideration, phyto-waste materials are highly considered to be a more important precursor because they are cost-effective, renewable nature, safe, available, and easily accessible sources. These waste residues are usually disposed of by burning or deposition in landfills, but conversion of phyto-waste to higher-value products would be preferable. Modified phyto-waste derived materials are extensively used as adsorbents for organic pollutants removal from pharmaceutical, textile, and food industries due to their highly porous structure, large adsorption capacity, simple regeneration, and extended lifetime.[19] In addition, modification of different phyto-waste materials has been growing interest because of their easy availability and also cost-effective. *Terminalia catappa* is a large tropical tree with porous and fibrous pericarp, hard endocarp enclosing the edible seed and whorled branches. This plant is mainly cultivated in the tropical regions of Asia, Africa, and Australia.[20] The fruit of this tree is known as 'Indian almond', comprises of kernel (10.32%), fibrous covering (8.97%), husk (34.08%), and hard endocarp (46.63%).[21] Apart from the natural biological cycle, huge amount of fruit shell (≈89%) is disposed as a phyto-waste.[22] It was convenient to propose an alternative phyto-waste strategy for the effective management of contaminants, *T. catappa* fruit shell and diclofenac from the environment. These approaches have considerable advantages in the aspect of both economic and environmental points of view. However, there was no report in the available literature on such material for diclofenac or other emerging pollutant removal.

The aim of the present investigation was to formulate a new alternative approach for the effective removal of diclofenac using modified phyto-waste, *T. catappa* fruit shell. In this study, *T. catappa* fruit shell was used as adsorbent for diclofenac removal after acid-thermal

modification. The modified *T. catappa* fruit shell (MTCFS) was characterized using Scanning Electron Microscope (SEM), Fourier Transform Infrared Spectroscopy (FT-IR) and Brunauer-Emmett-Teller (BET). Further, diclofenac adsorption experiment was performed in batch mode and isotherms, kinetics, and thermodynamic calculations were evaluated. Finally, desorption and reusability efficiency of MTCFS was assessed. The best of our knowledge, this is the first report on the adsorptive removal of diclofenac using modified phyto-waste.

2 Materials and methods

2.1 Adsorbate

Diclofenac sodium salt was purchased from Sigma-Aldrich. A stock solution of diclofenac was prepared by dissolving 1 g in 100 mL of deionized water and stored at 4 ˚C under dark condition. The stock solution was then appropriately diluted to make the desired diclofenac concentration in the working solution.

2.2 Adsorbent

The *T. catappa* fruit shells were collected and washed with deionised water. Then the washed fruit shell was cut into ≈50 mm pieces and was sun dried for 20 days. 500 grams of the cleaned and dried fruit shell powder was mixed with concentrated sulphuric acid in the ratio of 1:1 (w/v) in a 1000 mL glass bottle and heated for 12 h in a tubular furnace at 400 ˚C. Then, the modified material was rinsed with deionized water and dried for 6 h at 80 ˚C in hot air oven. The dried material was ground well using a grinder (Preethi Nitro Max, India) and sieved to obtain particle sizes within the range of 1.0-1.25 mm and was kept in an airtight container for further studies.

2.3 Structural characterization of MTCFS

The surface morphology and chemical properties of MTCFS were characterized using SEM, FT-IR and BET analysis. Microscopic images of the MTCFS were obtained by SEM analysis (JSM-5900, Jeol. Co., Japan). For analyses, the sample was coated with gold using a gold sputter at 10^{-1} M bar using a Bio Rad Polaron Division SEM coating system machine. The instrument was operated under the accelerating voltage of 2500.

FT-IR analysis (Perkin Elmer, USA) was used in order to determine the surface functional groups of the MTCFS by vibrational frequency changes in the functional groups, which were obtained by averaging the results of thirty-two scans in the range of 4,000-400 cm^{-1}. In order to avoid co-adsorbed water, the samples were dried under vacuum until constant weight and mixed with KBr (1:100) before the FT-IR spectrum was recorded.

The surface area was analysed from nitrogen adsorption/desorption isotherms measured at -194 ˚C (boiling point of nitrogen gas at atmospheric pressure) by the method of BET on a Micromeritics ASAP 2010 Surface Analyzer. Prior to gas adsorption measurements, the MTCFS was degassed at 200 ˚C in a vacuum condition for 4 h.

2.4 Batch experiment for diclofenac adsorption

Batch experiments for the diclofenac adsorption onto MTCFS in 50 mL of solution were studied with respect to well-established effective parameters including pH, temperature, adsorbent dosage, initial concentration of the adsorbate, and contact time at a constant speed of 160 rpm. Initially, the effect of pH on adsorption was studied over a pH range of 5 to 9 by agitating diclofenac solution (50 mg L^{-1}) with 50 mg L^{-1} of MTCFS at room temperature. The adsorption solution pH was adjusted with 0.1 M NaOH or HCl solutions. To investigate the

effect of temperature on adsorption process, the experiment was contacted with the solution consist of diclofenac (50 mg L^{-1}) and MTCFS (50 mg L^{-1}) under optimized pH condition on an incubator shaker at different temperature ranging from 20 to 50 ˚C with 10 ˚C increment. The adsorption experiment was performed with increasing amount of MTCFS up to 125 mg L^{-1} with diclofenac solution (50 mg L^{-1}) at optimized pH and temperature until equilibrium was reached, in order to know the effect of adsorbent dosage. To assess the effect of initial adsorbate concentration and contact time on adsorption process, the experiment with diclofenac concentration from 20 to 100 mg L^{-1} and the contact time up to equilibrium was studied under the optimized conditions noted above. The collected samples at a predetermined time were filtered using 50 µm pore size filtration membrane (Schleicher & Schuell Microscience) in order to minimize the interference of fine particles. The diclofenac concentration in the resulting filtrates was assessed using HPLC analysis. An HP 1200 (Agilent, USA) liquid chromatography equipped with 2.1 µm x 150 mm Eclipse C18 capillary column, particle size 3.5 µm (Agilent, USA) was used to determine the diclofenac concentration. The percentage of diclofenac adsorption was calculated using the following equation (1):

$$\text{Adsorption (\%)} = \frac{C_0 - C_e}{C_0} \text{ x } 100 \qquad (1)$$

where, C_0 is the initial concentration and C_e is the equilibrium concentration. Blanks were also performed simultaneously without MTCFS. All of the experiments were performed in duplicates and the mean values are presented in the results section of this paper.

2.5 Adsorption isotherms

The adsorption isotherms were used to design and optimize an operation procedure by equilibrium data which can be used to develop an equation for the comparison of the chosen

parameters. To examine the interaction between adsorbate and adsorbent concentrations at equilibrium, various adsorption isotherm models were applied to fitting the experimental data. The present study investigated with the Langmuir, Freundlich, Temkin, Dubinin and Redushkewich models. The Langmuir model is commonly used to quantify the adsorbate adsorbed onto adsorbent as a function of partial pressure or concentration at a given temperature. Particularly this adsorption model determines the monolayer type of adsorption in the experimental design. It is expressed as an equation (2) follows:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 K_L} + \frac{C_e}{Q_0} \quad (2)$$

where, K_L represents Langmuir equilibrium adsorption constant (L mg^{-1}) i.e. energy of sorption and Q_o (mg g^{-1}) is the Langmuir maximum sorption capacity i.e q_{max} (maximum amount of adsorbate adsorbed per gram of adsorbent). Linear plot of C_e/q_e against C_e was plotted and the values of Q_o (q_{max}) and K_L can be calculated from the slope and intercept of the graph. Separation factor, R_L was used to determine whether the adsorption process is favourable or unfavourable for Langmuir type of adsorption. The value of R_L was dimensionless constant which is calculated using the following equation (3):

$$R_L = \frac{1}{1+K_L C_0} \quad (3)$$

where, C_o is the initial concentration and K_L is the Langmuir constant. The value of R_L is used to find out the favourability of the adsorption system in which $R_L<1$ indicates a favourable adsorption while $R_L>1$, represents an unfavourable adsorption.

The Freundlich isotherm model is used to determine the adsorption intensity of the chosen adsorbent towards the adsorbate and the system heterogeneity and it expressed in the linearized form as follows:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \quad (4)$$

where, n represents the Freundlich constant, and it is related to the intensity of adsorption and to represent heterogeneity in the adsorption system. K_F (L mg^{-1}) is the Freundlich adsorption constant related to the adsorption capacity. A plot of log q_e against log C_e gives a straight line with a slope of $1/n$ and an intercept of K_F. Using the intercept value, n value was calculated.

The Temkin isotherm is used to assess the fall in the sorption heat and its logarithmic form is an equation (5) given as follows:

$$q_e = B \ln K_T + B \ln C_e \quad (5)$$

where, isotherm constant B (J mol^{-1}) is related to the heat of adsorption and K_T (L g^{-1}) is the equilibrium binding constant corresponding to the maximum binding energy which is estimated from the slope and the intercept of a plot of q_e versus ln C_e.

Dubinin and Redushkewich proposed an equation for mechanism with a Gaussian energy distribution onto a heterogeneous surface and to determine whether the adsorption occurred by physical or chemical process.[23] This isotherm equation (6) is given as:

$$\ln q_e = \ln q_{max} - \beta\varepsilon^2 \quad (6)$$

in this equation, q_e is the amount of diclofenac adsorbed (mg g^{-1}) and q_{max} is the maximum amount adsorbed under optimized experimental conditions; β is Dubinin-Radushkevich constant with dimension of energy, and can be calculated from adsorption potential (ε) by the following equation (7):

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \quad (7)$$

where, β is the mean free energy of sorption per mol of adsorbent (kJ mol^{-1}), ε is a term of polanyi potential, R is the gas constant (8.314 J mol^{-1} K^{-1}), T is the absolute temperature in K, and C_e is the equilibrium concentration (mol L^{-1}) of adsorbate solution. A plot of ln q_e versus ε^2 for various temperatures was employed to estimate the value of q_{max} and β.

Mean sorption energy (E) is the free energy transfer of one mole solute from infinity to the surface of adsorbent and was calculated by substitutes the values of β in the following equation (8):

$$E = \frac{1}{\sqrt{-2\beta}} \quad (8)$$

2.6 Kinetics studies

The kinetics studies were carried out using diclofenac solutions at concentrations of 20, 40, 60 and 100 mg L^{-1} at 30 ˚C for 2 h. The pseudo-first order equation can be represented as follows:

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \quad (9)$$

where, k_1 is the pseudo-first order rate constant (min^{-1}), q_t is the amount of solute adsorbed at time t (min) and q_e is the amount of solute (mg g^{-1}) adsorbed at saturation. The integrated form of the above equation is expressed as follows:

$$\log(q_e - q_t) = \log q_e - k_1 t \quad (10)$$

The values of q_e and k_1 can be calculated from the slope and intercept of the plots of log (q_e - q_t) versus t, respectively.

The adsorption kinetic data were examined using a pseudo-second-order reaction kinetics and expressed in the following equation (11):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (11)$$

where, k_2 (g out the spontaneous nature g^{-1} min^{-1}) is the pseudo-second-order rate constant; q_e is the amount of adsorbed at equilibrium (mg g^{-1}). The straight-line plot of t/q_t versus t is used to calculate the pseudo-second-order rate constant.

Chemisorption behaviour between adsorbate and adsorbent is examined by Elovich equation[24] and expressed as follows (12):

$$qt = \frac{1}{b}\ln(ab) + \frac{1}{b}\ln t \quad (12)$$

where, a (mg g^{-1} min^{-1}) is the initial sorption rate and b (mg g^{-1}) is represented the extent of surface coverage and activation energy in the chemisorption mode of interaction between adsorbate and adsorbent. The chemisorption kinetic will found to be linear if the interaction between adsorbate and adsorbent follows Elovich model. The values of (1/b) and (1/b) ln(ab) can be obtained from the slope and intercept of the linear plot drawn between qt versus ln t. The value of 1/b is represented the number of sites available for adsorption and the (1/b) ln(ab) value indicated the adsorption quantity when ln t is equal to zero.[24]

Diffusion is one of the rate limiting factors in the adsorptive removal of diclofenac. Weber and Morris[25] proposed intraparticle diffusion model and it can be used to determine the intraparticle diffusion rate constant (k_p) can be obtained from the following equation (13):

$$q_t = k_p t^{1/2} + C \quad (13)$$

where, k_p and C represents the intraparticle diffusion rate constant (mg g^{-1} $min^{1/2}$) and the thickness of the boundary layer. The boundary layer effect was greater, if larger the C value. Plot of q_t versus $t^{1/2}$ is a straight line which passes through the origin when the intraparticle diffusion is

the limiting stage of the adsorption, but if it is not passing through the origin, then the intraparticle diffusion is not only the rate limiting step and also the external mass transfer played an important role in the adsorption process. It is concluded that the two or more individual steps are vital role in the adsorption process.[26,27]

2.7 Thermodynamic parameters

The thermodynamic parameters of adsorption process were evaluated with various initial concentrations (20 to 100 mg L^{-1} of diclofenac) at different temperature (20, 30 to 40 ˚C) for 2 h. Parameters such as Gibbs free energy (ΔG^o), the heat of the adsorption (ΔH^o) and standard entropy changes in the systems (ΔS^o) are assessed to find out the spontaneous nature of the system, to determine its exothermic or endothermic nature of the adsorption process and to evaluate the changes in randomness of the system. The interaction effect of size ratio (n) and lateral coefficient (α) at solid-liquid interface was considered for the adsorption using the following equations (14-17):

$$\left(\frac{\theta e^{-2\alpha\theta}}{(1-\theta)^n}\right) = kC_e \quad (14)$$

$$K = \frac{e^{(-\Delta G/RT)}}{55.5} \quad (15)$$

$$\ln K = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (16)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (17)$$

The Gibbs free energy (ΔG^0) was calculated from the following models: the Frumkin, the modified Frumkin, the Flory-Huggins, and the Langmuir. The logarithmic form of the equation (18) is as follows:

$$\ln\theta - \ln(1-\theta)^n C_e = 2\alpha\theta + \ln K \quad (18)$$

The degree of surface coverage (θ) can be calculated by following equation (19):

$$\theta = \frac{q_e}{q_{e(max)}} \quad (19)$$

where, q_e and $q_{e(max)}$ represents the amount adsorbed at equilibrium and the maximum adsorption capacity of the adsorbate, respectively. Linearized forms of Frumkin, modified Frumkin, Flory-Huggins, and Langmuir isotherm models can be obtained by substituting the *n* and *α* pair values of 1,1; 2,1; 2,0; and 1,0 respectively, into equation 18 and obtained following expression (eq. 20-23):

$$\ln \frac{\theta}{C_e(1-\theta)} = 2\theta + \ln K \quad (20)$$

$$\ln \frac{\theta}{C_e(1-\theta)^2} = 2\theta + \ln K \quad (21)$$

$$\ln \frac{\theta}{(1-\theta)} = \ln C_e + \ln K \quad (22)$$

$$\ln \frac{\theta}{(1-\theta)^2} = \ln C_e + \ln K \quad (23)$$

To calculate (ΔG_0), logarithmic form of equation (24) was used as follows:

$$\ln K = -\frac{\Delta G}{R}.\frac{1}{T} - \ln 55.5 \quad (24)$$

2.8 Desorption and reusability

Desorption experiment was performed in order to know the regeneration capacity of the adsorbent for reuse. The spent MTCFS (100 mg) was separated from the solution by centrifugation and used for the desorption study. The diclofenac desorption experiment was performed by continuous agitation of the diclofenac loaded MTCFS at pH 5 and 60 ˚C under 200 rpm. The filtrate was analysed for the concentration of diclofenac desorbed from MTCFS. The

reusability efficiency of MTCFS was assessed over several cycles. After the adsorption, the adsorbate loaded adsorbent from each cycle were regenerated by desorption and reintroduced into a fresh adsorption cycle. The percentage of adsorption was measured at the end of each cycle as mentioned in section 2.4. These experiments were carried out in duplicates and the data's were presented in the result corresponds to the mean values with a standard error.

3 Results and discussion

3.1 Structural characterization of MTCFS

The SEM image of MTCFS is shown in Fig. 1a. The image clearly revealed the smooth surface texture with homogeneous porous structure. The BET analysis result shows the surface area of the MTCFS is found to be 514 $m^2 g^{-1}$. This surface area is little smaller than some of the adsorbent materials like carbon black (1443 $m^2 g^{-1}$) [28] and activated carbon (950 $m^2 g^{-1}$) [29], that have been used to remove diclofenac. Nevertheless, our result is superior to other agro-waste materials, such as rice husk (0.69 $m^2 g^{-1}$) [30], rice bran (0.46 $m^2 g^{-1}$) [31], grape bagasse (2 $m^2 g^{-1}$) [12]. Fig.1b illustrates the FT-IR spectrum of diclofenac, MTCFS and diclofenac loaded MTCFS. The IR spectrum of diclofenac showed that the peaks appeared at 1283.39 cm^{-1} and 1305.57 cm^{-1} attributed to C–N stretching, whereas peaks at 1507.10 cm^{-1} and 1575.56 cm^{-1} resulted from C=C stretching and C=O stretching of carboxyl group, respectively. Intensity band between 3600 and 3000 cm^{-1} denotes hydroxyl (O–H) group stretching which appeared in the spectrum of diclofenac as similarly reported by Nayak and Pal.[32] In the spectrum of MTCFS, intensity band around 3500 cm^{-1} is typically corresponds to the hydroxyl groups and other absorption peaks at 2925, 1450, 1685, ~1100, 1000–1100, 1150–1200 are attributed to C–H (alkyl), C–C (aromatic) C=C, C=O (aldehyde/ketone), C–O (alcohols), C–X (fluoroalkanes), C–O (alcohols) groups, respectively. The characteristic absorption bands of diclofenac at C–N

stretching, carboxyl group and hydroxyl (O–H) group stretching vibrations appeared in the spectrum of diclofenac loaded MTCFS, which indicated the successful adsorption of diclofenac into MTCFS. The intensity of the hydroxyl and carbonyl bands slightly increased in the diclofenac loaded MTCFS, which indicates physical adsorption of adsorbate onto adsorbent. In addition, no relevant changes were observed in the structural vibration region of MTCFS after adsorption of diclofenac thereby confirmed the structural stability of MTCFS after diclofenac adsorption.

3.2 Batch adsorption experiment

In general, adsorption process is mainly depending on the solution pH, because this process influenced by electrostatic and/or non-electrostatic interaction. Keeping the field applicability of pH condition in mind the present study performed between pH 5 to 9. Fig. 2a illustrates the effect of different pH on diclofenac adsorption onto MTCFS. The results confirmed that the adsorption was pH dependent and the maximum adsorption was attained at pH 5. The diclofenac adsorption was considerably decreased from 89% at acidic (pH 5) to 51% at basic conditions (pH 9). According to Attia *et al*.[33] that the adsorbate becomes a neutral molecule at pH below its dissociation constant (pKa) value and interacts with the adsorbent through non-electrostatic interactions. In the case of pH above the pKa value, the surface of adsorbate exhibits negative charge and leading to an electrostatic repulsion between them. Diclofenac has a pKa of 4.0±0.2 at 25 ˚C; thus, adsorption was much decreased at basic pH condition. According to Cuerda-Correa *et al*.[28] that the dissociation degree of the surface groups of the adsorbent is high and also both of the adsorbent and the solutes occur as negatively charged forms at basic pH values. Consequently, the adsorption is not efficient due to the electrostatic repulsions between adsorbate and surface of the adsorbent. Therefore, this study proved pH played a significant role

on sorption and MTCFS have excellent ability for diclofenac removal at pH 5. The pH 5 is slightly higher than the pKa value of diclofenac; however, much more difference in the diclofenac adsorption was not observed between pH 4 and 5. Consequently, pH 5 was selected as the optimum condition for all adsorption experiments. Similar results were reported for the adsorption of diclofenac using granular activated carbon Calgon Filtrasorb 400,[10] magnetic nanoparticles coated zeolite,[33] and molecularly imprinted polymer microspheres.[9]

The effect of temperature on diclofenac adsorption onto MTCFS is shown in Fig. 2b and it was observed that the adsorption efficiency decreased when the treatment temperature increases. This is may be due to the increase in the solubility of adsorbate, resulted in a stronger interaction force between adsorbate and solute than the interaction between adsorbate and adsorbent.[34] The formation of intermolecular hydrogen bonding between the adsorbate and adsorbent also play a significant role in the adsorption process; however, these existing bonds broken at elevated temperature. This result is directly interpreted to the increasing Brownian movement of molecules in solution.[35] Moreover, the functional group present in the surface of MTCFS may not be active at low temperature. Therefore, adsorption efficiency was decreased at 20 ˚C. Therefore, further adsorption studies were performed at 30 ˚C.

The effect of adsorbent dosage was assessed by varying dosage of MTCFS between 25 to 125 mg L^{-1} as shown in Fig. 2c. It can be seen that the diclofenac adsorption efficiency was increased from 36 to 89% with increasing adsorbent dosage from 25 to 100 mg L^{-1}, and then it remains constant. This increasing adsorption might be due to the availability of the surface area with more adsorptive sites at higher adsorbent dosage.[36] However, the amount of diclofenac adsorbed per unit mass of the adsorbent decreased considerably. The decrease in unit adsorption

with increasing dose of adsorbent may be due to the adsorption sites remaining unsaturated during the adsorption process.[37]

To study the effect of initial concentration of adsorbate and the adsorbent-adsorbate contact time, the adsorption experiment was performed with different initial concentrations of diclofenac (20-100 mg L^{-1}) until equilibrium was reached and the result is depicted in Fig. 2d. The results show that the maximum diclofenac adsorption was decreased with increasing initial concentration. This is may be due to the increase in the mass transfer driving force. Similar results were reported for the adsorption of 2-Picoline onto activated carbon prepared from almond shell and orange peel.[38] The amount of diclofenac adsorbed onto MTCFS was increased along with the increase in contact time. However, the contact time exceeded 2 h, the uptake was gradually decreased, which indicated that the equilibration time was around 2 h. The amount of diclofenac adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under these operating conditions. It is proved that the MTCFS is efficient in attaining equilibrium gradually. The result shows that the adsorption was more rapid in the beginning; however, it gradually decreased with time until it reached equilibrium. It might be due to the availability of the unoccupied surface area of the adsorbents.[39,40] Recently, Aljeboree *et al*.[41] and Sathishkumar *et al*.[19] also reported similarly that the rate of adsorption onto activated carbon prepared from phyto-residues were higher in the beginning for other organic substances.

3.3 Adsorption isotherm modeling

In this study, Langmuir, Freundlich, Dubinin Redushkewich, and Temkin isotherms were studied for diclofenac adsorption onto MTCFS. Langmuir isotherm was employed in order to know the monolayer adsorption of the adsorbate. Fig.3a-c corroborated that the Langmuir isotherm was well fitted and their constants are derived from the slope and intercept of the plot.

These results show that the diclofenac was adsorbed as monolayer onto MTCFS. The maximum adsorption capacity of the MTCFS was calculated as q_0 (q_{max}) and it was found to be 90.6, 96.1 and 78.5% for at 20, 30 and 40 ˚C, respectively, under optimized conditions. This result confirmed that the chosen adsorbent was effectively adsorbed the diclofenac from aqueous solution at 30 ˚C. The implication of low values of intercept corresponds to the binding energy (K_L) of the sorption, which reflects the binding affinity of the adsorbent towards the chosen adsorbate. Separation factor, R_L for diclofenac was found to be less than 1 for the temperature of 20, 30 and 40 ˚C which confirmed that the present adsorption system is favorable for the uptake of diclofenac for the chosen initial concentrations (20 to 100 mg L^{-1}) (Table 1 and Fig 3d). Further, this result describes that the temperature played a key role in the determination of adsorbent affinity toward the selected adsorbate. The maximum adsorption capacity was observed at 30 ˚C which is similar to the report of Antunes *et al*.,[12] who reported that decreased diclofenac adsorption on grape bagasse while increasing temperature. It has been deduced from the current study that the temperature range above 30 ˚C can destabilize the affinity between adsorbate and adsorbent. Similarly, Karaman *et al*.[42] also achieved 98 to 100 % diclofenac adsorption using micelle–clay and activated carbon at 27 ˚C. Khaskheli *et al*.[43] observed maximum diclofenac adsorption up to 25 ˚C, thereafter absorbance was gradually decreased.

The K_F values determined from Freundlich isotherm were used to compare the adsorption capacity of the adsorbent tested at different temperatures. The result shows that Freundlich $1/n$ values were less than unity suggesting that MTCFS has the heterogenous nature of the surface and it is favourable for the diclofenac adsorption process.[44] The value of n greater than 1 for diclofenac indicates positive cooperativity in binding with MTCFS. Regression values suggested that the temperature at 20 and 30 ˚C was linear than 40 ˚C by comparing their R^2. Furthermore,

K_F values suggested that the increased capacity of the adsorbent for diclofenac adsorption at 30 ˚C and beyond which there was a marked decrease in diclofenac adsorption. It has been predicted from Freundlich isotherm that the adsorption of diclofenac mostly occurs as multilayer phenomenon. Comparing the *n* value in Freundlich isotherm model, it was slightly higher at 30 ˚C than 20 and 40 ˚C. It can ascribe due to increased heterogeneity in the system as clearly seen from Table 2 and Fig. 4 which implied that increased temperature beyond 40 ˚C and below 20 ˚C, the adsorption rate, K_F was decreased and even though *n* value increased (1.22, 1.38, and 3.65, respectively) at 40 ˚C, its maximum adsorption capacity, K_F was very low. Thus, Freundlich isotherm indicated the maximum rate of adsorption, and positive interaction for binding of diclofenac was achieved at 30 ˚C. The present investigation proved that 30 ˚C was suitable temperature for the removal of diclofenac. The equilibrium time of diclofenac was attained within 2 h up to 94 % of removal and this is the less equilibrium time with maximum removal ever reported in literature. Furthermore, it was stated that the grape bagasse required maximum of 24 h to reach equilibrium and 48 h for granular activated carbon to remove diclofenac.[45,46] The equilibrium time of the MTCFS was higher than that of the grape bagasse; [12] however, the diclofenac removal efficiency was considerably higher in the present report. These results confirm that the MTCFS is a potential candidate for the adsorption of emerging micropollutants like pharmacologically active compounds (PhACs) including diclofenac.

Dubinin Radushkewick isotherm model was used to determine the type of interaction occurred during the adsorption process. Table 2 illustrated the Dubinin Radushkewick isotherm model for calculating *E* values at various temperature ranges. Generally, values of free energy change (mean sorption energy, *E*) which occurred due to transfer of one mole of the ion from infinity in the solution to the surface of the solid was found to be in the range from 1 to 8 kJ mol^{-}

[1] which indicated that the adsorption process is physical in nature and values between 8 and 16 kJ mol^{-1} is meant for the ion-exchange mechanism and values greater than 16 kJ mol^{-1} was considered to be controlled by particle diffusion mechanism.[47,48] In the present study, the obtained *E* values were found to be in the range of 2.91-3.83 kJ mol^{-1} and confirmed that the adsorption process is achieved through physical in nature and there is no possibility of physico-chemical or ion exchange mechanism in adsorption process. The regression coefficient showed the high sorption capacity up to 30 ˚C (Table 2). Thus, the present study demonstrated that physisorption was the main mechanism for the adsorption of diclofenac into adorbate.

Linear plots of Temkin isotherm are shown in Table 2. This model illustrated that maximum binding energy, K_T values were found to be decreased with increasing reaction temperature. Bajpai *et al*.[49] reported that well fitted R^2 was observed only at 30 ˚C for the diclofenac adsorption. This result explains that the increasing temperature might be affecting the diclofenac adsorption process. It has been stated that uniform binding energies required for the effective interactions between diclofenac and MTCFS surface. The binding energy (K_T) calculated from Temkin model indicated that the increasing temperature decrease the quantity of adsorbed diclofenac on the MTCFS surface.

3.4 Kinetic studies

Fig. 5a-d and Table 3 showed the kinetic adsorption behaviour of diclofenac onto MTCFS. The results evident that pseudo-second-order was well fitted in good linearity in term of R^2 (0.98) than pseudo-first-order. It is noteworthy that the calculated and experimental values are similar in pseudo-second-order than the pseudo-first-order kinetic model as well as Elovich model. The smaller values of binding constant indicated a faster adsorption while larger rate constant, k_1 usually represents more rapid adsorption.[50] In this study, among the obtained k_1 (0.3-1.75 x 10^{-4} L

min^{-1}) and k_2 (7.23 - 0.93 x 10^{-4} g mg^{-1} min^{-1}), rate constant value k_1 represented faster adsorption of the diclofenac onto MTCFS; but, k_1 predominantly suitable for low concentrations.

Fig. 5c depicts Elovich model to describe chemisorptions behaviour related to diclofenac adsorption. The regression coefficients (R^2) were relatively low and represented unfitness of the model. This indicated that the chemisorptions behaviour was not observed in the adsorption of diclofenac and did not influence on the reaction rate, since the Dubinin Radushkewick isotherm model indicated the adsorption of diclofenac was mainly through physical mode. This result confirmed that the sorption system is not kinetically followed either pseudo-first order or Elovich model while the pseudo-second order sorption mechanism is dominant. Similar type of result was reported for the adsorption of PhACs onto the activated carbon.[51-53] Furthermore, the result revealed that the second order kinetic is mostly prevalent in adsorption processes in which rate-controlling step is an exchange reaction.[54]

The diffusion mechanism in the pores is significance to explain the rate limiting step in the adsorption system. In the dynamic process, there are three stages were considered to be rate limiting step while studying the interaction between solid-solution system.[55] The first one is film diffusion in which adsorbate molecules moved to the external surface of the adsorbent and the second step is prevailing pore diffusion or intraparticle diffusion in which transport of adsorbate molecules to the adsorption site or the liquid filled pores of the adsorbent. The third step is internal or external diffusion mechanism in which an interaction of the adsorbate molecules was categorized based on the type of the binding process. Among the aforementioned steps, the slowest one is the rate limiting step and also it influences the adsorption process. The first two steps are the key steps or rate limiting steps since the third one is not considered in rate limiting step because of interaction at the active site is extremely fast and the overall rate of adsorption is

only controlled by either film or intraparticle diffusion or by the combination of both.[56-58] As shown in Fig.5d, the straight line did not pass through the origin which revealed intraparticle diffusion mechanism is not a rate limiting step in adsorption. It has been suggested from intraparticle diffusion that surface adsorption and intraparticle diffusion mechanism were simultaneously operating during the diclofenac adsorption. Even though, the straight line was not passed to the origin, its k_p values calculated from the slope (9.02 to 2.18) were an indication of enhanced adsorption behaviour exhibited by the prepared adsorbent for the initial concentrations of the adsorbate.[59] It also explained about the existence of an improved binding between the diclofenac and MTCFS. The higher value of C indicated an enhancement in the rate of adsorption and showed increasing in the boundary layer thickness. The C values derived from the plot of q_t versus $t½$ were higher than 1 and found to be significant for the chosen adsorbent. Increasing concentration of adsorbate is directly altered in C values and it exemplified an increase in the rate of adsorption thereby increase in the boundary layer thickness.[12] The suitable explanation is that a high concentration of the adsorbate dissolved in the water increases the resistance to mass transfer from the surrounding of adsorbent surface.[45] Regression coefficient, R^2 showed that the current adsorption system was found to be in accordance with the selected initial concentrations.

3.5 Thermodynamic studies

Temperature is considered to be a critical factor for the adsorption process as shown in fig 2b. The experiments conducted at different temperature showed the percentage of diclofenac adsorption decreased as the temperature increases. The results showed that the equilibrium time was not altered by temperature, which revealed that equilibrium is independent of temperature

(Table 2). It is noticed that the temperature exerted greater influence in the adsorption of diclofenac.

Variation in the adsorption rate of diclofenac with the effect of temperature (20, 30, and 40 ˚C) was explained in terms of free energy change (ΔG_0), enthalpy (ΔH_0) and entropy (ΔS_0) of the system. The ln k values are obtained from intercepts of Frumkin, modified Frumkin, Flory-Huggins, and Langmuir isotherm models by drawing linear plots between $\ln\frac{\theta}{(1-\theta)C_e}$ and θ, $\ln\frac{\theta}{(1-\theta)^2 C_e}$ and θ, $\ln\frac{\theta}{(1-\theta)^2}$ and $\ln C_e$, and $\ln\frac{\theta}{(1-\theta)}$ and $\ln C_e$. Plots of ln k versus $1/T$ for the Frumkin, modified Frumkin, the Flory-Huggins, and the Langmuir isotherm models give an idea about good regression values.

The values for Gibbs free energies in the adsorption of diclofenac (ΔG_0) with 20, 30, and 40 ˚C were obtained from slopes of Frumkin, modified Frumkin, the Flory-Huggins, and the Langmuir isotherm models which were found to be -25.931, -33.126, -19.887 and -7.899, respectively. The negative values of ΔG_0 corroborated that spontaneous nature of the adsorption process and also suggested absence of energy barrier during the adsorption process. The negative enthalpy (ΔH_0) values (-0.009, -0.051 and -0.052) for the chosen temperature indicated the adsorption process was an exothermic in nature. Hence, elevation in temperature would disturb affinity and diclofenac binding potential with adsorbent at equilibrium. This trend was confirmed from the decreased $q_{\max}$ values of Langmuir and Freundlich isotherm model when the temperatures increased to 40 °C. The positive values of the entropy (ΔS_0) (1.81, 6.65 and 7.78) was an indication of the occurrence of the increased randomness at the solid-solution interface in adsorption process and also suggested the decreasing affinity of the adsorbent to diclofenac. Moreover, it has been noticed in diclofenac adsorption that randomness in the solid–solution

interface was increased when the temperature rose.[12] This result was similar to the report of Suriyanon *et al*.,[55] who did the diclofenac adsorption onto functionalised silica-based porous materials. The attributed reason is the occurrence of an energy barrier during the adsorption process and the solubility of the diclofenac in water. The energy barrier possibly arose from the repulsion between adsorbent and diclofenac. Thus, the positive entropy value ascribed to a conclusion that instability in adsorption process and structural change in diclofenac at solid-liquid interface at elevated temperature. Furthermore, the positive values of entrophy showed structural changes in the adsorbate and adsorbent during adsorption of diclofenac. Solubility of the diclofenac increased when the temperature increased and this in turn raises the affinity of the diclofenac towards solvent than the adsorbent. Therefore, elevated temperature increase the hindrance between diclofenac and adsorbent and also caused the increase in the agitation of the dissolved adsorbate thereby reducing the adsorption rate.[12] It has been proved that the release of the heat into the solution in the adsorption process; thus, the adsorption process is considered to be exothermic in nature and change free energy value was indicative of spontaneous, temperature influenced adsorption of diclofenac. It is concluded that the increase in temperature decreases the adsorption of diclofenac thereby equilibrium switched to the inverse direction of the reaction.

3.6 Desorption and reusability

In order to reuse the diclofenac adsorbed MTCFS, desorption experiment was performed at 60 ˚C with continuous agitation of the system. The results revealed that the above 92% of diclofenac was desorbed from MTCFS after 6 h (Fig. 6a). This reversible process might be due to the weak hydrogen bond between the adsorbate and adsorbent as well as a stronger interaction force between adsorbate and solute at elevated temperature.[34] Hence, at high agitation (200 rpm) the diclofenac will be diffused into the solution. Fig. 6b illustrates that the reusability of MTCFS

against diclofenac adsorption. The results showed the adsorption efficiency of MTCFS was maintained up to eight reuses with 85% of removal, after that gradually decreased to 50% in 12th cycle. This continuous recyclic application process for micropollutant removal could be added value to the phyto-waste MTCFS as a potential adsorbent. Sotelo *et al.*[60] reported that the cost of the commercial activated carbon is a relatively high cost, not an efficient adsorbent for diclofenac, and also shows difficulties in the possibilities of the regeneration. Therefore, in an economic point of view, the MTCFS adsorbent could be cheaper than the commercial absorbent in terms of availability and cost-of preparation for practical applications.

4 Conclusions

This study concluded that the potential applicability of MTCFS for the removal of diclofenac from aqueous solution. Batch experiments proved that temperature and pH are mainly influenced the adsorption process. Adsorption process followed the Langmuir isotherm model verified the monolayer adsorption and adsorption was found to be favourable. The maximum adsorption capacity was found to be at 30 ˚C. Temkin isotherm model revealed that that increasing temperature affected the adsorption of diclofenac. Type of interaction in the adsorption process was determined by Dubinin Radushkewick isotherm model which implied that the present adsorption system achieved through physical interaction. Pseudo-second-order kinetic model was well fitted for the diclofenac adsorption. Intraparticle diffusion results indicated that increasing in the rate of adsorption and increase in the boundary layer thickness. Spontaneous nature of the adsorption process was supported by the negative values of ΔG_0 which indicated the absence of energy barrier for the adsorption process. This is the special aspect of MTCFSas adsorbent for the better removal of diclofenac. This is the first reported for the diclofenac with above 90% removal capacity. Thus, wastewater contaminated by diclofenac was treated with low-cost

agricultural wastes to neutralize the toxicity effect rendered by diclofenac. This bench scale experiments would be helpful to develop a model system to treat such kind of emerging pharmaceutically active compounds.

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Figure legends

Fig. 1 (a) SEM image of MTCFS and (b) FT-RI spectrum of MTCFS, diclofenac, and diclofenac loaded MTCFS.

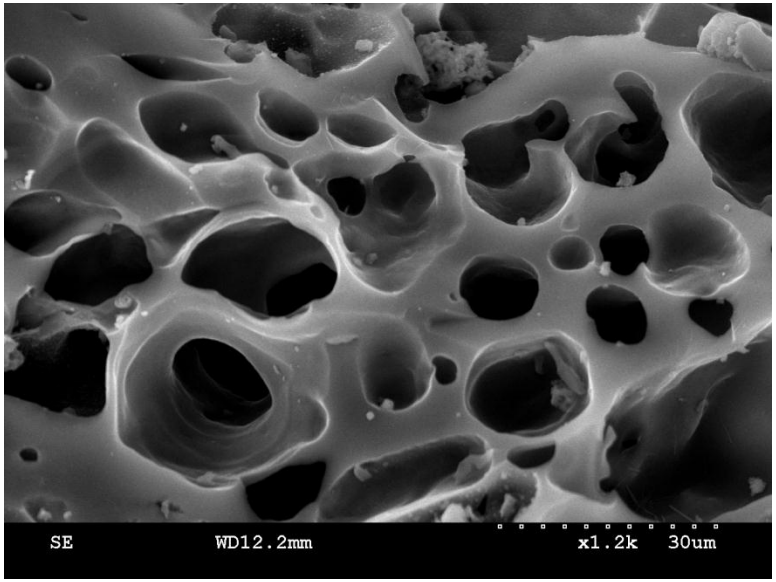
Fig. 2 Effect of (a) pH, (b) temperature, (c) adsorbent dosage, and (d) adsorbate initial concentration with different contact time on diclofenac adsorption onto MTCFS.

Fig. 3 Langmuir isotherms for adsorption of diclofenac onto MTCFS at (a) 20 °C, (b) 30 °C, and (c) 40 °C and (d) R_L value at studied temperature.

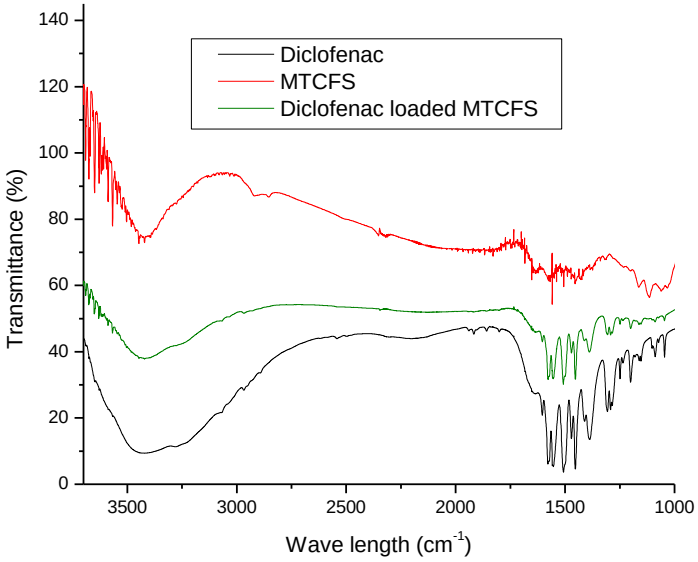
Fig. 4 Freundlich isotherms adsorption of diclofenac onto MTCFS at (a) 20 °C, (b) 30 °C, and (c) 40 °C.

Fig. 5 Kinetic models of (a) Pseudo-first order, (b) Pseudo-second order, (c) Elovich isotherm model, and (d) Intraparticle diffusion model for the adsorption of diclofenac onto MTCFS.

Fig. 6 (a) Desorption and (b) Reusability of MTCFS for diclofenac removal.



(a)



(b)

Fig. 1

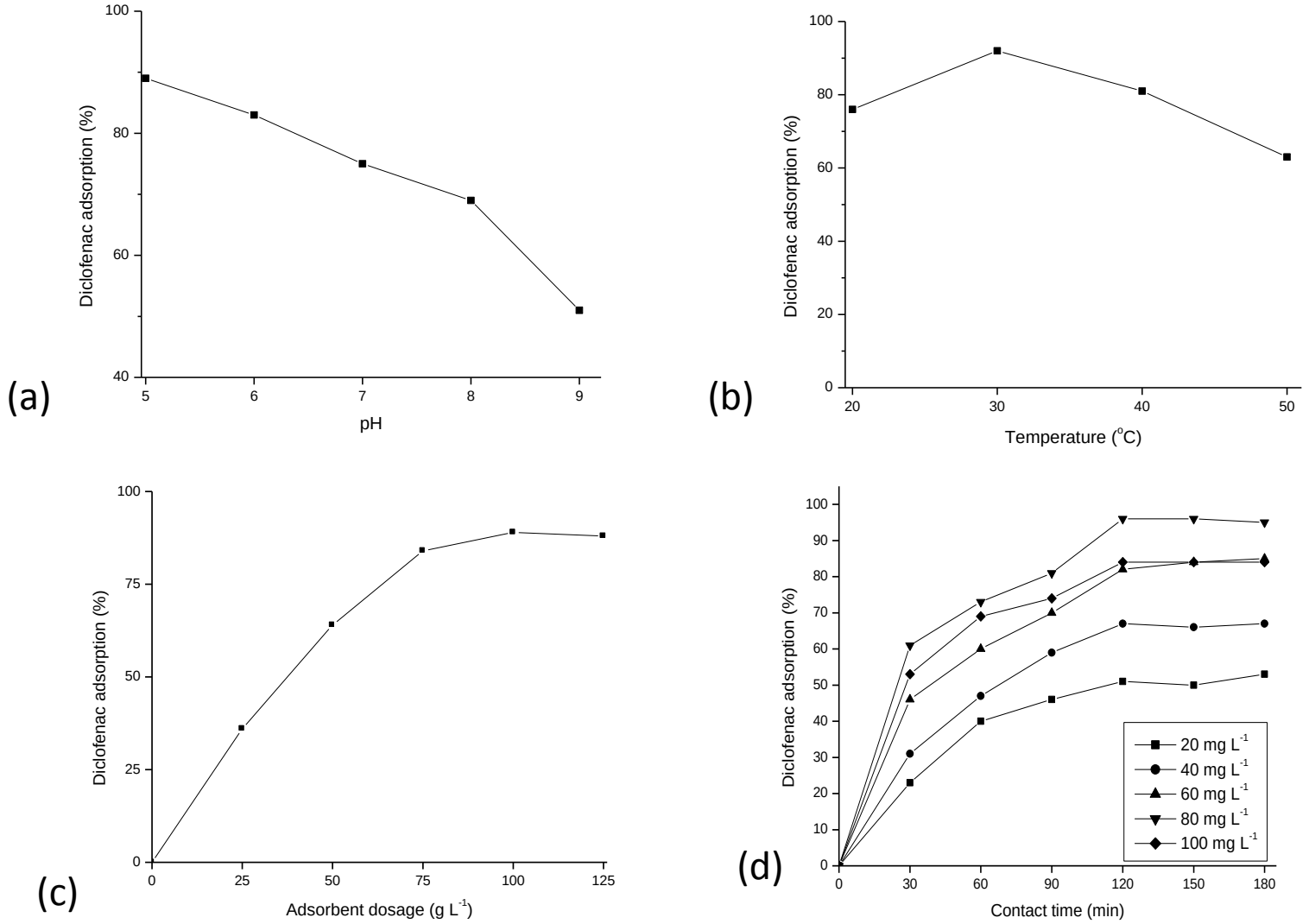
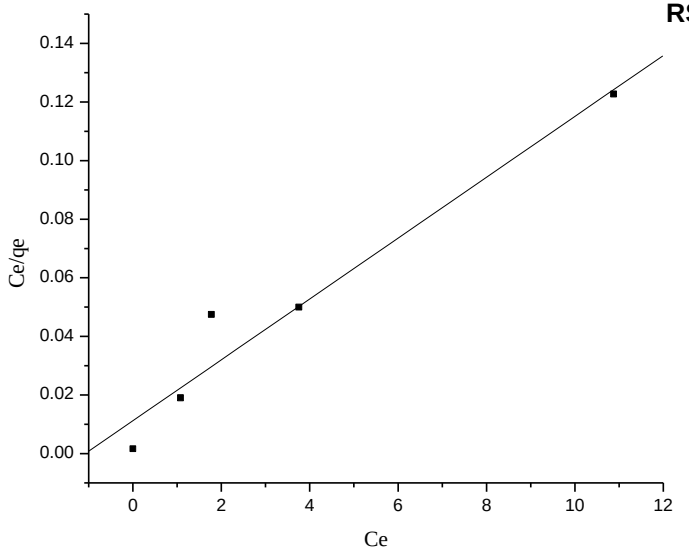


Fig. 2

(a)



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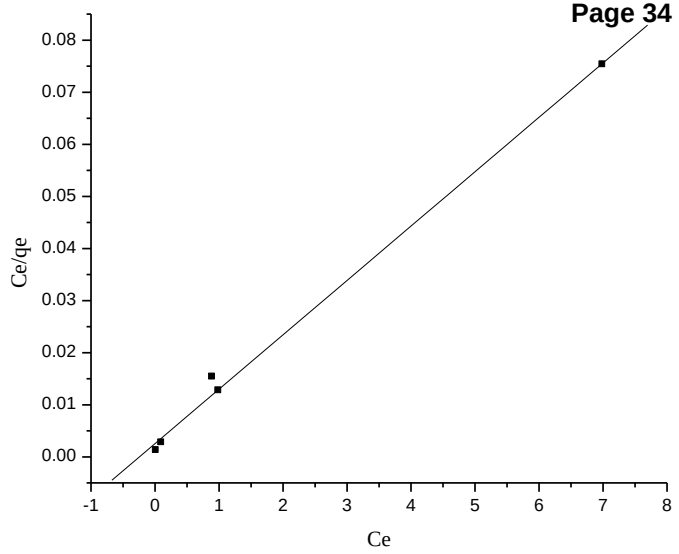

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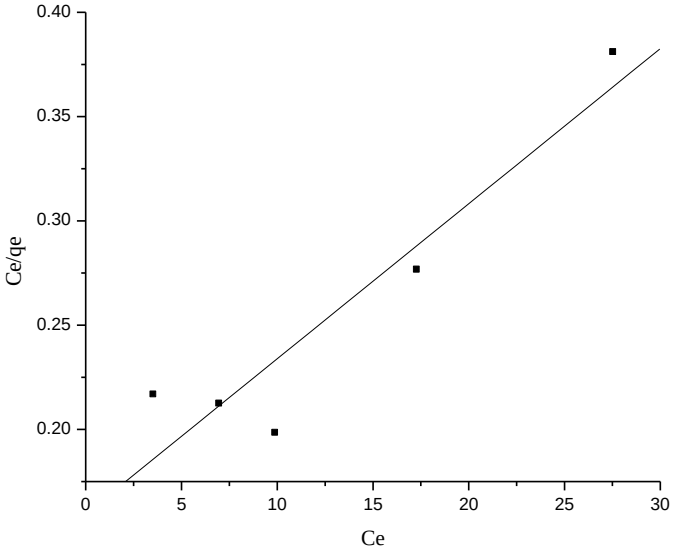


(d)

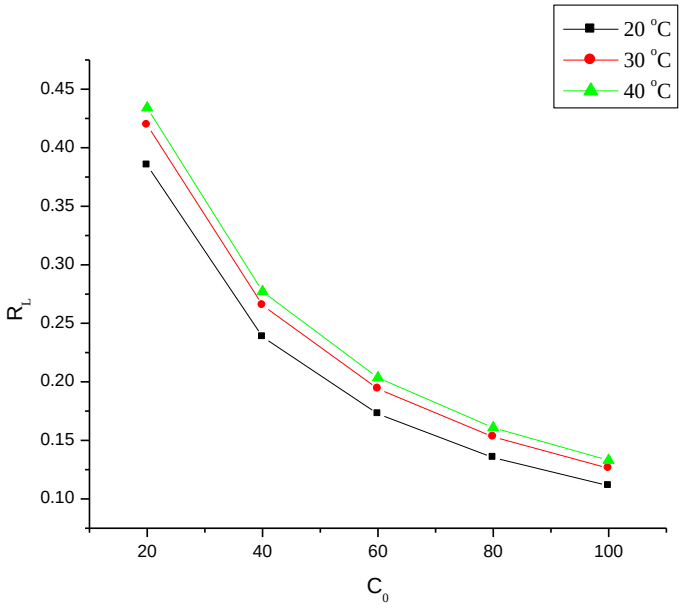


Fig. 3

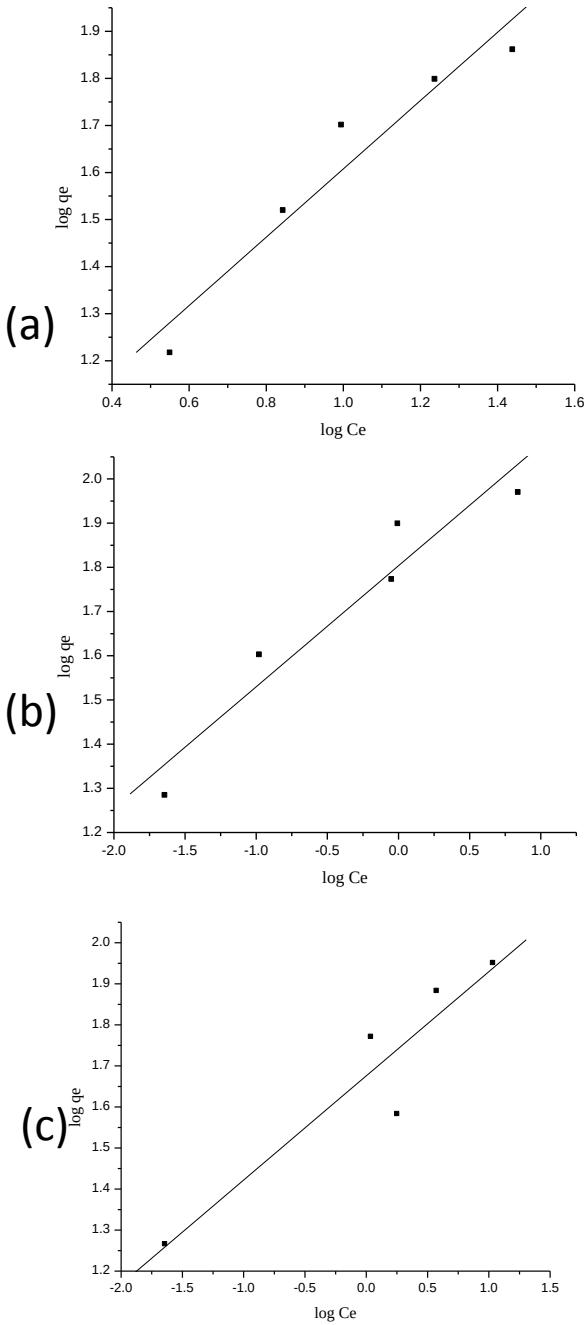
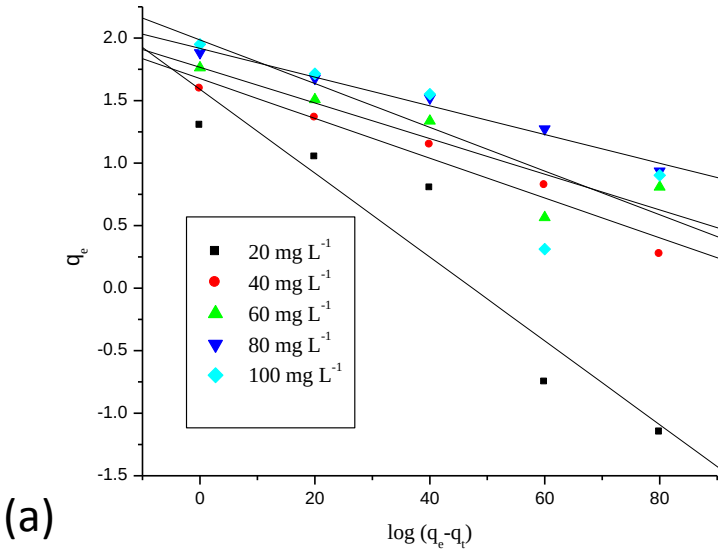
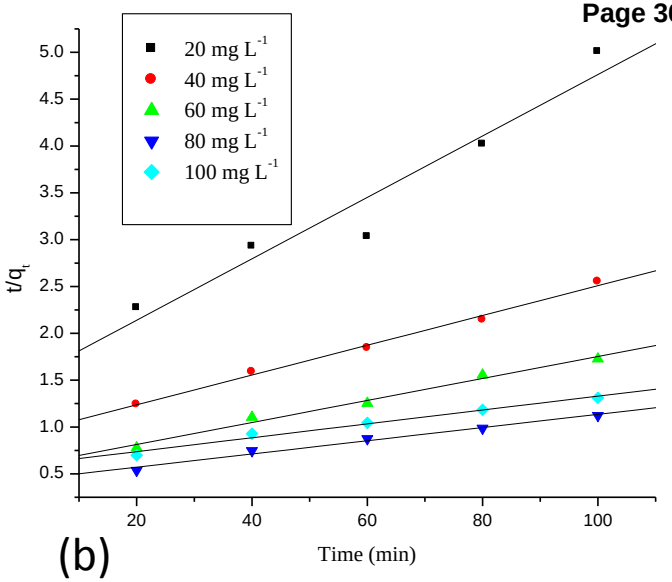


Fig. 4



(a)



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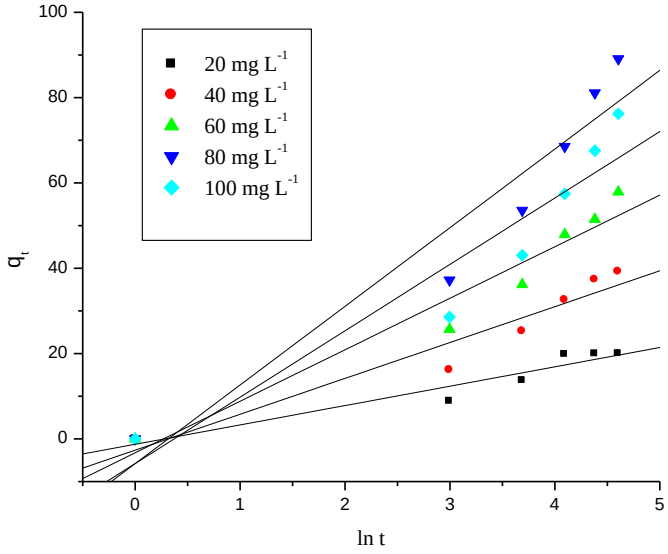

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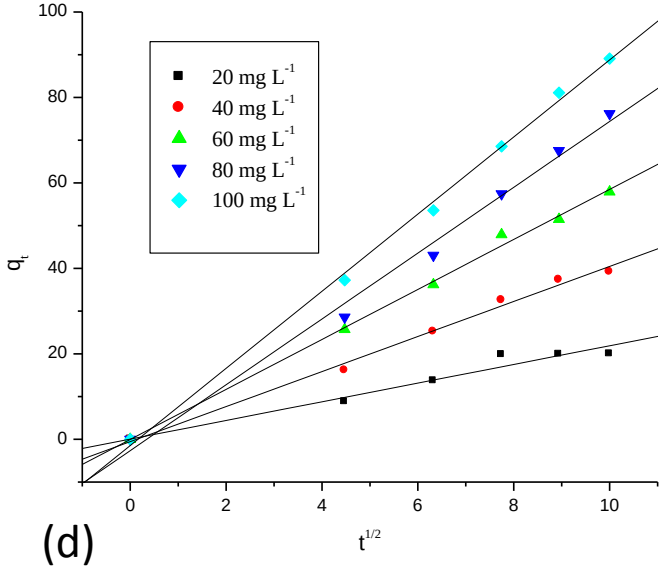

(d)

Fig. 5

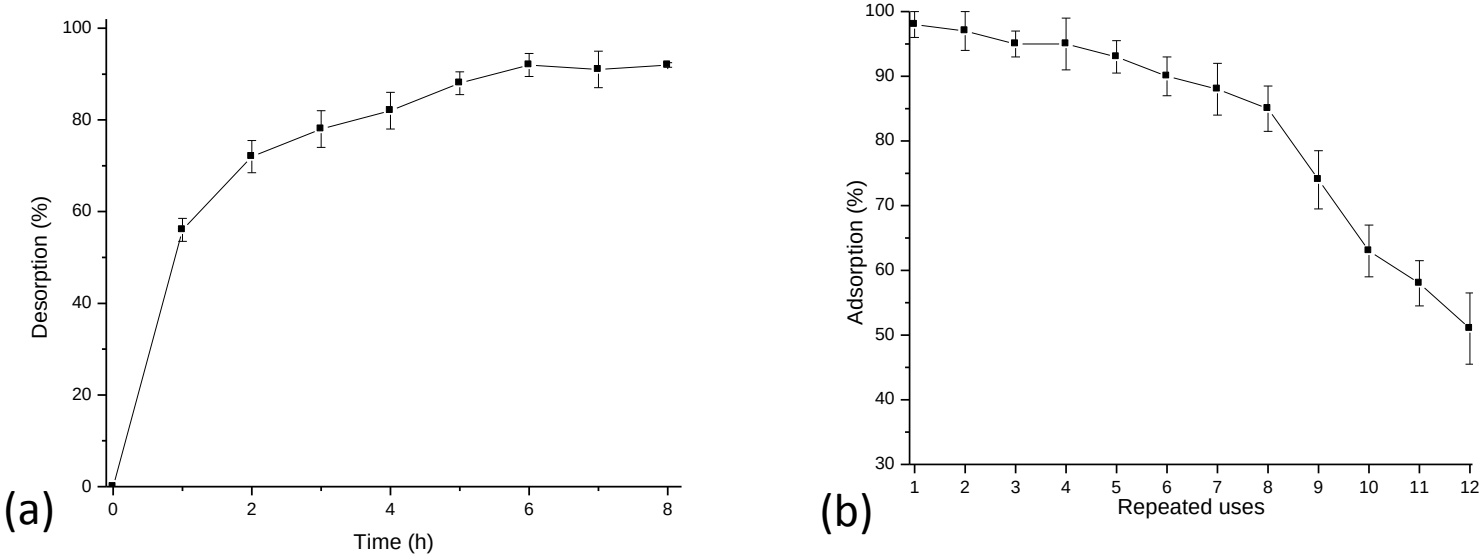

Fig. 6

Table 1 Langmuir isotherm constants and their R_L values

Temperature	Langmuir isotherm constant			R_L value for different initial concentrations				
	Q_{max} (mg g^{-1})	K_L (L mg^{-1})	R^2	20 mg	40 mg	60 mg	80 mg	100 mg
20 °C	90.6	0.07	0.95	0.16	0.09	0.06	0.05	0.04
30 °C	96.1	0.08	0.95	0.42	0.27	0.19	0.15	0.13
40 °C	78.5	0.07	0.92	0.37	0.23	0.17	0.13	0.11

Table 2 Various isotherm models and their values at different temperature

Temperature	Freundlich model			Dubinin Radushkewick model			Temkin model		
	K_F (L mg^{-1})	n	R^2	E (kJ mol^{-1})	q_{max}	R^2	B (J mol^{-1})	K_T (L g^{-1})	R^2
20 °C	47.41	1.22	0.93	2.92	1.4 x 10^{-3}	0.94	28.17	18.87	0.98
30 °C	63.63	1.38	0.96	3.10	3.4 x 10^{-4}	0.95	0.89	2.88	0.94
40 °C	7.62	3.65	0.92	3.83	5.0 x 10^{-3}	0.76	0.39	1.22	0.8

Table 3 Kinetics constants for the adsorption of diclofenac

Pseudo-first order model constants					Pseudo second order model constants				Intraparticle diffusion model		Elovich model
C_0	q_e, exp (mg g^{-1})	q_e, cal (mg g^{-1})	K_1(mi n^{-1})	R^2	Q_e exp (mg g^{-1})	Qe cal (mg g^{-1})	K_2 (g mg^{-1} min^{-1})	R^2	Kp (mg g^{-1} $min^{1/2}$)	R^2	R^2
20	19.97	38.91	0.3	0.16	19.98	19.05	7.23×10^{-4}	0.94	9.02	0.96	0.92
40	39.2	47.42	1.59	0.61	39.2	38.24	2.75×10^{-4}	0.99	7.7	0.99	0.93
60	57.9	58.38	1.21	0.99	57.9	57.99	2.36×10^{-4}	0.98	5.85	0.99	0.94
80	76.22	82.61	1.65	0.64	76.2	77.11	1.17×10^{-4}	0.98	4.1	0.99	0.92
100	89.1	96.68	1.75	0.68	89.1	89.75	0.93×10^{-4}	0.98	2.18	0.99	0.90