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**ORIGINAL RESEARCH**

Removal of sodium diclofenac from aqueous solutions by rice hull biochar

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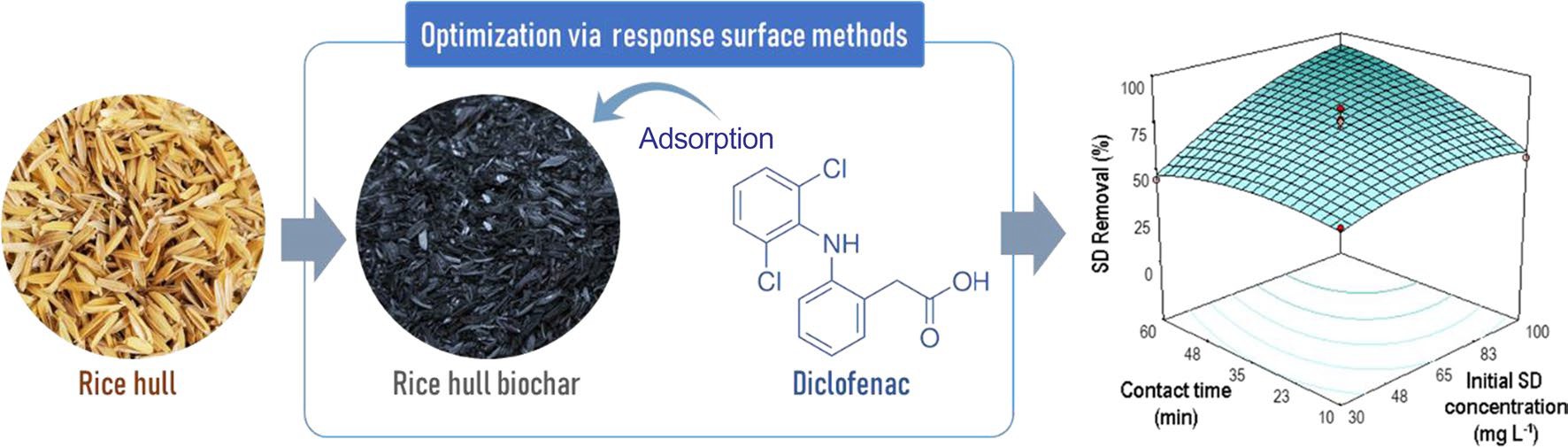
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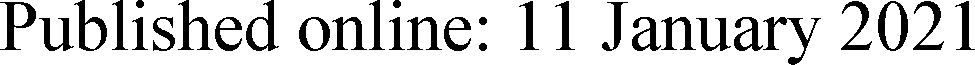
**Abstract**

Diclofenac is an ecotoxic pharmaceutical compound affecting both aquatic and terrestrial ecosystems even at low concentra- tions. In this study, batch adsorption experiments were conducted to remove sodium diclofenac (SD) from aqueous solutions using rice hull biochar (RHB) adsorbents. Higher SD removals were obtained with increasing initial SD concentration, RHB dosage, contact time, and decreasing initial pH. Isotherm studies revealed that Langmuir isotherm best fitted the experimental data with the highest coefficient of determination for both pH 2 (*R2* = 0.9827) and pH 7 (*R2* = 0.9460). For kinetic studies, the pseudo second-order model gave *R2* = 0.9999 for both pH 2 and pH 7. SD removals reached up to 97% at pH 2 and up to 80% at pH 7. Higher SD removals were achieved at solution pH lower than the adsorbent pHpzc since electrostatic repulsion was eliminated. Fourier-transform infrared analysis showed the major involvement of C=O in the adsorption process. This study demonstrated the potential of using agricultural residues such as rice hulls for the treatment of wastewater contami- nated with pharmaceutical compounds.

**Graphic abstract**



**Keywords** Adsorption · Biochar · Isotherm · Kinetics · Rice hull · Sodium diclofenac

**Nomenclature**

*C0* Initial SD concentration, mg L−1

*C* Final SD concentration, mg L−1

*Q* Equilibrium adsorption capacity, mg g−1

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*qm* Maximum adsorption capacity, mg g−1

*b* Energy of adsorption, L mg−1

*Ce* Equilibrium concentration of the adsorbate, mg L−1

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*RL* Separation factor or equilibrium parameter *Kf* Freundlich capacity factor, (mg1−1/*n* L1/*n* g−1) *1/n* Intensity parameter

*β* Constant related to heat of sorption, J mol−1

*α* Temkin isotherm equilibrium binding constant, L g−1

*qt* Amount of adsorbate at contact time *t*, mg g−1

*k1* Pseudo-first-order rate constant, min−1

*k2* Pseudo-second-order rate constant, g mg −1 min−1

*kid* Intraparticle diffusion rate constant, mg g−1 min−0.5

# Introduction

Pharmaceuticals and personal care products (PPCPs) are emerging contaminants that have been a cause for concern in recent years (Hu et al. [2011](#_bookmark40)). Extensive use of PPCPs, such as analgesics, antibiotics, contraceptives, lipid regula- tors, insect repellents, sunscreens, lotions, soaps, toothpaste, detergents, fragrances, and skin, hair, and dental care prod- ucts, both in medical and veterinary practice has resulted in their presence in unaltered form in surface waters (Martínez et al. [2011](#_bookmark54); Liu and Wong [2013](#_bookmark52)), since these persistent com- pounds are not removed completely by sewage treatment plants (STPs) and other conventional treatment methods (Gotostos et al. [2014](#_bookmark36)). When these compounds are released into recipient waters, they can be bioaccumulated and, there- fore, may present potential risks to human health and aquatic organisms (Sotelo et al. [2012](#_bookmark64)).

Among the pharmaceutical substances that reach the aquatic environments via industrial effluents and human use, sodium diclofenac (SD) is the most widely detected (Wu et al. [2019](#_bookmark74)). Chemically known as sodium 2-[(2,6-dichlo- rophenyl) amino] phenyl] acetate, SD is among the most extensively-used nonsteroidal anti-inflammatory drugs (NSAIDs) (Ensano et al. [2017](#_bookmark31)). In fact, this drug is widely used to treat livestock especially across the Indian sub- continent (Green et al. [2004](#_bookmark37)). The global consumption of diclofenac is estimated to be 940 tons per year, with detec- tion concentration in surface waters, groundwaters, and even in drinking waters in the range of ng L−1 to μg L−1 in the last years (Malefane et al. [2019](#_bookmark53)). Extensive studies on SD metabolism in humans and animals have been conducted (Fei et al. [2006](#_bookmark32); Tiwari et al. [2015](#_bookmark68)), and it was discovered that after ingestion, unchanged diclofenac, together with its hydroxylated metabolites, are excreted by the body through urine and feces (Stülten et al. [2008](#_bookmark65)). These compounds enter wastewater treatment plants (WWTP) where the removal percentage of SD typically ranges from 21% to 40% during the treatment processes (de Luna et al. [2017](#_bookmark28)).

The adverse effects of these pharmaceutical compounds, such as SD, which has been proven to be ecotoxic and affects both aquatic and terrestrial ecosystems (Oaks et al. [2004](#_bookmark58)),

have led to strict regulations that require the elimination of pharmaceutical residues from industrial wastewaters. PPCPs are commonly removed from wastewaters by membrane fil- tration (de Luna et al. [2019](#_bookmark29)), advanced oxidation processes (Lin et al. [2016](#_bookmark51)), photodegradation (Paragas et al. [2018](#_bookmark62)), and adsorption (Abo El Naga et al. [2019](#_bookmark17)). However, the large-scale application of these technologies is hindered by the high cost of installation. Among the various treatment systems for pharmaceutical wastewaters, adsorption is by far one of the most promising. In particular, the use of biochar as sorbent material addresses the high cost of commercially available activated carbon.

Biochar is a carbonaceous product of biomass thermal conversion under low-oxygen environment (Kim et al. [2020](#_bookmark46)). It is the prime product of torrefaction at 200–300 °C, and a pyrolysis by-product at 300–600 °C (Genuino et al. [2018](#_bookmark35); Arriola et al. [2020](#_bookmark20)). It is an organic-rich material that is effective in the adsorption of pharmaceuticals (Genu- ino et al. [2017](#_bookmark34)). Availability, abundance, low cost, and the renewable nature of the adsorbent material, along with the simple preparation method and ease of process operations, are among the advantages of this technology (Antunes et al. [2012](#_bookmark18); Ifthikar et al. [2017](#_bookmark41)). Several agricultural wastes and other materials like municipal solid wastes have been used as biochar precursors for decontaminating industrial/domestic wastewater (Sumalinog et al. [2018](#_bookmark66)). A particularly abun- dant agricultural waste that can be used for biochar produc- tion is rice hull, which is the residue obtained from the rice milling process. While rice hulls have been used as fuel in boiler furnaces of various industries to produce steam, these agricultural residues have limited or no practical use in the Philippines. The annual generation of rice hulls exceeds 140 million tons worldwide, 96% of which comes from develop- ing countries (Kalderis et al. [2008](#_bookmark44)). Since the rice industry is expected to continue for a long time, with predicted total rice consumption at 450 million tons by 2020 (milled basis) (Lim et al. [2012](#_bookmark50)), the availability of rice by-products will remain high. Thus, utilization of rice hull as adsorbent can add value to this waste material and significantly contribute to effec- tive waste management. Several studies have reported on the application of rice hull biochar (RHB) for dye (Khan et al. [2020](#_bookmark45)) and heavy metals (Han et al. [2020](#_bookmark38)) removal. However, the application of RHB for the removal of SD from water matrices has not yet been fully explored.

Biochar adsorbents derived from rice hulls were previ-

ously prepared in various researches at temperatures ranging from 270 °C to 700 °C (Leksungnoen et al. [2019](#_bookmark49); Shi et al. [2019](#_bookmark63)), with some studies utilizing a variety of modifications, such as microwave-assisted pyrolysis, steam activation, acid activation, alkaline activation, CO2 activation and electro- chemical modification (Wang et al. [2020b](#_bookmark73)). However, rice hull adsorbents may also be prepared through torrefaction at lower temperatures (200–300 °C) (Arpia et al. [2021](#_bookmark19)) and

without modifications or use of chemical activating agents (de Luna et al. [2013](#_bookmark26)). This process conforms with the essen- tial advantages of using biochar as adsorbents which are low cost and compatibility with green manufacturing (Wang et al. [2018](#_bookmark71)). Compared with biochar modification processes that require high activation temperatures and chemical acti- vating agents, the process used in this study is more eco- nomical, requires low energy consumption, and is environ- ment friendly.

The study aims to determine the applicability of RHB in removing SD from aqueous solutions. Parametric studies were done to determine the effects of operating parameters

after 24 h of contact time for which the value of pH equilib- rium was reached. This value was approximately equal to the adsorbent pHpzc.

Sample SD concentrations were determined following the study by Matin et al. ([2005](#_bookmark56)). SD-containing samples (2 mL) were combined with 1 mL concentrated nitric acid (HNO3 63% w/v, Merck) to produce a yellowish compound diluted to 10 mL with distilled water. The absorbance of the resulting solution was read at maximum wavelength (λmax) of 365 nm using a UV–Vis spectrophotometer (Model UV 1601, Shimadzu). Diclofenac removal was computed using the following equation:

such as initial SD concentration, RHB dosage, initial solu-

*C* − *C*

tion pH, and contact time on SD removal. Box–Behnken design (BBD) was used to determine the optimum condi- tions of these parameters. Isotherm and kinetic studies were employed to identify the best-fitting models, as well as the dominant mechanism of the adsorption process.

SD Removal (%) = 0 × 100.

*C*0

## 2.3 Batch adsorption experiments: optimization, isotherm, and kinetic studies

(1)

# Materials and methods

## Preparation of SD aqueous solutions and rice hull adsorbents

All chemicals used in this study were of analytical grade. A synthetic SD stock solution (500 mg L−1) was prepared by

Erlenmeyer flasks containing 20 mL samples of varying initial SD concentrations, RHB dosage, initial pH, and con- tact time were agitated using a magnetic stirrer at 300 rpm and 25 °C. The pH of the solution was adjusted with 0.1 M sodium hydroxide (NaOH 99%, Merck) and 0.1 M hydro- chloric acid (HCl 99%, Merck). Box–Behnken design with three levels was used to optimize process parameters,

dissolving diclofenac sodium salt (C H Cl NNaO , 99%,

namely initial SD concentration (30, 65, 100 mg L−1), RHB

14 10 2 2

dosage (0.1, 0.3, 0.5 g), initial pH (2, 5.5, 9), and contact

Sigma-Aldrich) in distilled water. Working SD solutions were prepared by diluting the stock solution with distilled water.

Rice hulls were obtained from a rice mill in Muñoz, Nueva Ecija, Philippines. The rice hulls were washed thor- oughly with distilled water to remove particles and water- soluble impurities. The washed hulls were dried in an oven at 100 °C for 30 min and pulverized in a Thomas-Wiley laboratory mill. The powdered hulls were sieved to obtain

time (10, 35, 60 min). Adsorption experiments were carried out at optimum conditions. For the isotherm study, SD solu- tions of different initial SD concentrations (20, 40, 60, 80, and 100 mg L−1) were prepared at pH 2 and pH 7. Kinetic studies were conducted at varying durations (10, 20, 30, 40, 50, and 60 min). All the experiments were performed in triplicates. The adsorption capacity (*Q*) was computed using the following equation:

particles that were 300–500 μm in size and severely torre- fied in an oven at 350 °C for 1 h. The RHB powder was then stored in clean and dry containers.

## Analytical methods

The elemental compositions of raw rice hulls (RRH) and RHB were examined by energy dispersive X-ray analysis (EDX, TM-1000, Hitachi). The functional groups involved

*Co* − *C* volume of solution

*Q* = .

mass of adsorbent

# Results and discussion

## Adsorbent characterization

(2)

in SD adsorption were analyzed by Fourier-transform infra- red (FTIR) spectroscopy (Nicolet 6700, Thermo Scientific). The point-of-zero charge (pHpzc) was determined by mass titration method that used increasing amounts of RHB added to water to obtain suspensions of 0.01, 0.1, 1, 5, 10, and 20% by weight. These samples were agitated for 24 h and then filtered. The final pH of each suspension was measured

Raw rice hulls contain cellulose, hemicellulose, lignin, extrac- tives, water and mineral ash. The mineral content include oxides of silicon, potassium, magnesium, iron, aluminum, and calcium (Nakbanpote et al. [2000](#_bookmark57)). Figure [1](#_bookmark0) shows that RRH was composed mainly of carbon (16.53 wt%), oxygen (40.51 wt%), and silicon (42.96 wt%). Similar findings were previ- ously reported (Souza et al. [2002](#_bookmark30)). After severe torrefaction,

Si

CaO C

K

**Rice hull biochar**

Fe

O

Ca K K Ca

Fe

Si

C

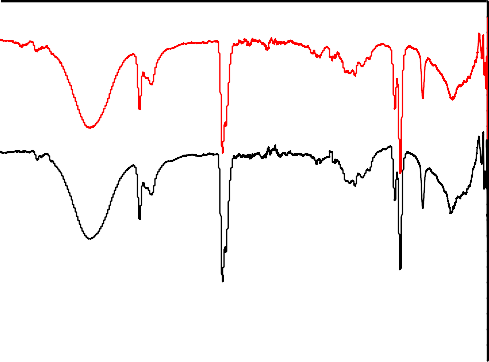
**Raw rice hulls**

**0 1 2 3 4 5 6 7**

**Intensity (a.u)**

**keV**

**Fig. 1** EDX atomic composition of raw rice hulls (RRH) and rice hull biochar (RHB)



**After adsorption**

**Before adsorption**

**Transmittance (a.u)**

-C=O

Si-O-Si

**4000 3500 3000 2500 2000 1500 1000 500**

O-H, N-H

C-H

C=C

-C-O

aromatic C-H

Si-O

**Wavenumber (cm-1)**

**Fig. 2** FTIR spectra of RHB before and after adsorption

other elements from the mineral ash, such as potassium, cal- cium, and iron, were liberated and exposed. In addition to this, the atomic composition of carbon significantly increased from 25.3% to 40.48% after torrefaction, thus making RHB a more effective adsorbent compared to RRH (Nakbanpote et al. [2000](#_bookmark57); Wang et al. [2001](#_bookmark70); Souza et al. [2002](#_bookmark30)).

The results of the FTIR analysis of RHB before and after adsorption are shown in the FTIR spectra presented in Fig. [2](#_bookmark1). The broad peak at 3300–3400 cm−1 corresponds to the stretching of –OH groups due to SiOH and adsorbed water (de Luna et al. [2013](#_bookmark26)). The peak at 3000 cm−1 and those

1700 cm−1, which corresponds to C=O stretching vibrations, resulted in the largest shift to 1900 cm−1 after SD adsorption (Coates [2000](#_bookmark23); Jeon [2011](#_bookmark43)). This indicates that the stretching of the C=O in the carbonyl or carboxyl groups participated the most in the SD adsorption process (Yu et al. [2013](#_bookmark75)).

## Optimization of the adsorption parameters

In this study, Box–Behnken design (BBD) was used to investigate the effects of important operating parameters in the removal of SD using RHB adsorbent, and to determine the optimum condition for SD adsorption. BBD is a type of response surface method (RSM) which is based on a three-level incomplete factorial design, and requires fewer runs compared to other RSM designs (de Luna et al. [2012](#_bookmark25)). From Box–Behnken design, the highest SD removal was 97% using the following experimental conditions: initial SD concentration = 100 mg L−1, solution pH = 2, RHB dos- age = 0.3 g and contact time = 35 min (Table [1](#_bookmark3)). In contrast, the lowest SD removal was 41% at initial SD concentra- tion = 65 mg L−1, pH = 9, RHB dosage = 0.1 g and contact time = 35 min. This is consistent with the findings on the effect of varying initial solution pH on SD removal.

The results of the analysis of variance (ANOVA) pre- sented in Table [2](#_bookmark4) show that the response surface quadratic model obtained was significant, with model *F*-value at 9.93. This indicates that the model can explain most of the vari- ations in the response (de Luna et al. [2015](#_bookmark27)). The high coef- ficient of determination (*R2*) of 0.9145 and an adjusted *R2* value of 0.8224 indicate that the quadratic model is reliable in predicting responses. Likewise, all main parameters (ini- tial SD concentration, RHB dose, initial pH, and contact time) and the interactions between initial SD concentration and contact time were significant, with *p* values of less than

0.05. Three-dimensional (3D) response surface plot (Fig. [3](#_bookmark5)) was generated using RSM to show the significant interaction effects between contact time and initial SD concentration. As observed, longer contact time and higher initial SD con- centration resulted in higher SD removal. This is attributed to the increased interaction between SD molecules and the available binding sites on the RHB surface.

The quadratic model equation in terms of coded factors is expressed by the following equation:

*Y* =76.797 + 13.262*X*1 + 6.999*X*2 − 14.921*X*3 + 6.899*X*3

+ 5.655*X X* + 5.037*X X* + 9.311*X X* + 2.816*X X*

1

2

1

3

1

4

2

3

at 2100–2400 cm−1 are attributed to C–H stretching and

− −4.000*X X* + 1.379*X X* 6.914*X*2 − 4.964*X*2

C≡C stretching, respectively. Indications of aromatic C–H

2 4 3 4 1 2

−1 − +0.452*X*2 − 5.911*X*2,

and C–O stretching are seen in the peaks at 800–1000 cm 3 4

and 1000–1100 cm−1, respectively (de Luna et al. [2013](#_bookmark26)).

(3)

Si–O bond stretching vibration is also observed in the peak at 700 cm−1 (Chen et al. [2012](#_bookmark22)). In addition, the peak at

where *Y* is the predicted response variable for SD removal and *X1*, *X2*, *X3* and *X4* correspond to the independent

**Table 1** BBD for SD removal using RHB

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Run | *X1:* Initial  SD conc (mg L−1) | *X2:* RHB  Dosage (mg) | *X3:* Initial pH | *X4:* Contact Time (min) | Actual  SD removal (%) | Predicted  SD removal (%) |
| 1 | 30 | 100 | 5.50 | 35 | 50 | 48 |
| 2 | 100 | 100 | 5.50 | 35 | 71 | 63 |
| 3 | 30 | 500 | 5.50 | 35 | 42 | 51 |
| 4 | 100 | 500 | 5.50 | 35 | 86 | 89 |
| 5 | 65 | 300 | 2.00 | 10 | 80 | 79 |
| 6 | 65 | 300 | 9.00 | 10 | 41 | 46 |
| 7 | 65 | 300 | 2.00 | 60 | 93 | 90 |
| 8 | 65 | 300 | 9.00 | 60 | 60 | 62 |
| 9 | 65 | 300 | 5.50 | 35 | 83 | 75 |
| 10 | 65 | 300 | 5.50 | 35 | 70 | 75 |
| 11 | 30 | 300 | 5.50 | 10 | 55 | 51 |
| 12 | 100 | 300 | 5.50 | 10 | 57 | 59 |
| 13 | 30 | 300 | 5.50 | 60 | 45 | 46 |
| 14 | 100 | 300 | 5.50 | 60 | 85 | 91 |
| 15 | 65 | 100 | 2.00 | 35 | 74 | 81 |
| 16 | 65 | 500 | 2.00 | 35 | 91 | 89 |
| 17 | 65 | 100 | 9.00 | 35 | 41 | 45 |
| 18 | 65 | 500 | 9.00 | 35 | 70 | 65 |
| 19 | 65 | 300 | 5.50 | 35 | 77 | 75 |
| 20 | 65 | 300 | 5.50 | 35 | 83 | 75 |
| 21 | 30 | 300 | 2.00 | 35 | 82 | 81 |
| 22 | 100 | 300 | 2.00 | 35 | 97 | 98 |
| 23 | 30 | 300 | 9.00 | 35 | 45 | 41 |
| 24 | 100 | 300 | 9.00 | 35 | 81 | 78 |
| 25 | 65 | 100 | 5.50 | 10 | 52 | 52 |
| 26 | 65 | 500 | 5.50 | 10 | 76 | 74 |
| 27 | 65 | 100 | 5.50 | 60 | 76 | 74 |
| 28 | 65 | 500 | 5.50 | 60 | 84 | 80 |
| 29 | 65 | 300 | 5.50 | 35 | 72 | 81 |
| 30 | 65 | 300 | 5.50 | 35 | 76 | 81 |

variables: initial SD concentration, RHB dosage, initial pH and contact time. From Eq. ([3](#_bookmark2)), higher initial SD concentra- tion, RHB dosage, and contact time and lower initial pH will result in better SD removals. Table [1](#_bookmark3) also shows the proximity of the predicted and actual percent SD removals, confirming the reliability of the quadratic model.

The numerical optimization of process parameters achieved a 96% SD removal (predicted) at 100 mg L−1 initial SD concentration, 0.5 g of RHB dose and pH 2. At this con- dition, the residual SD concentration was found at 4 mg L−1 and the adsorption capacity was at 3.3 mg g−1. Experimental validation of the model at optimum conditions resulted in 95.5% SD removal, 3.6 mg L−1 residual SD concentration and adsorption capacity of 3.4 mg g−1. Based on the percent error (0.52% for SD removal), the model generated is robust and reliable (de Luna et al. [2015](#_bookmark27)).

## Factors affecting SD removal

The effect of initial pH of the water matrix on SD removal is shown in Fig. [4](#_bookmark8)a. The highest SD removals were obtained at pH 2 for both 0.1 and 0.5 g RHB dosages. It is evident from Fig. [4](#_bookmark8)a that SD removal decreased as the solution pH was raised, with the lowest removal observed at pH 7. The pH point-of-zero charge (pHpzc) of RHB is at pH 6.21, as deter- mined by mass titration. At pH 2 (pH < pHpzc), the surface of the RHB is positively charged, whereas at pH 7 (pH > pHpzc), it is negatively charged (de Luna et al. [2017](#_bookmark28)). Furthermore, SD is an acid and has a dissociation constant (pKa) value of 4.15. At pH < pKa, the SD molecules are positively charged, while at the pH > pKa, these molecules are nega- tively charged (de Luna et al. [2017](#_bookmark28)). Thus, at pH 7 where the solution pH was greater than both the adsorbent pHpzc and

**Table 2** ANOVA for the response surface model for SD removal using RHB

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Source Sum of squares *df* Mean square *F* value | | | | | *p* value |  |
|  |  |  |  |  | Prob > *F* |
| Model | 7237.57 | 14 | 516.97 | 9.93 | < 0.0001 | Significant |
| *X1*—initial SD conc. (mg L−1) | 2107.25 | 1 | 2107.25 | 40.48 | < 0.0001 | Significant |
| *X2*—RHB dosage (mg) | 588.00 | 1 | 588.00 | 11.30 | 0.0051 | Significant |
| *X3*—initial pH | 2671.49 | 1 | 2671.49 | 51.32 | < 0.0001 | Significant |
| *X4*—contact time (min) | 571.11 | 1 | 571.11 | 10.97 | 0.0056 | Significant |
| *X1X2* | 127.91 | 1 | 127.91 | 2.46 | 0.1410 | Not significant |
| *X1X3* | 101.48 | 1 | 101.48 | 1.95 | 0.1860 | Not significant |
| *X1X4* | 346.74 | 1 | 346.74 | 6.66 | 0.0228 | Significant |
| *X2X3* | 31.72 | 1 | 31.72 | 0.61 | 0.4490 | Not significant |
| *X2X4* | 64.00 | 1 | 64.00 | 1.23 | 0.2876 | Not significant |
| *X3X4* | 7.61 | 1 | 7.61 | 0.15 | 0.7084 | Not significant |

*2*

*X*

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| 327.81 | 1 | 327.81 | 6.30 | 0.0261 | Significant |
| 168.95 | 1 | 168.95 | 3.25 | 0.0948 | Not significant |
| 1.40 | 1 | 1.40 | 0.027 | 0.8723 | Not significant |
| 239.62 | 1 | 239.62 | 4.60 | 0.0514 | Not significant |

*1*

2

*X*

*2*

2

*X*

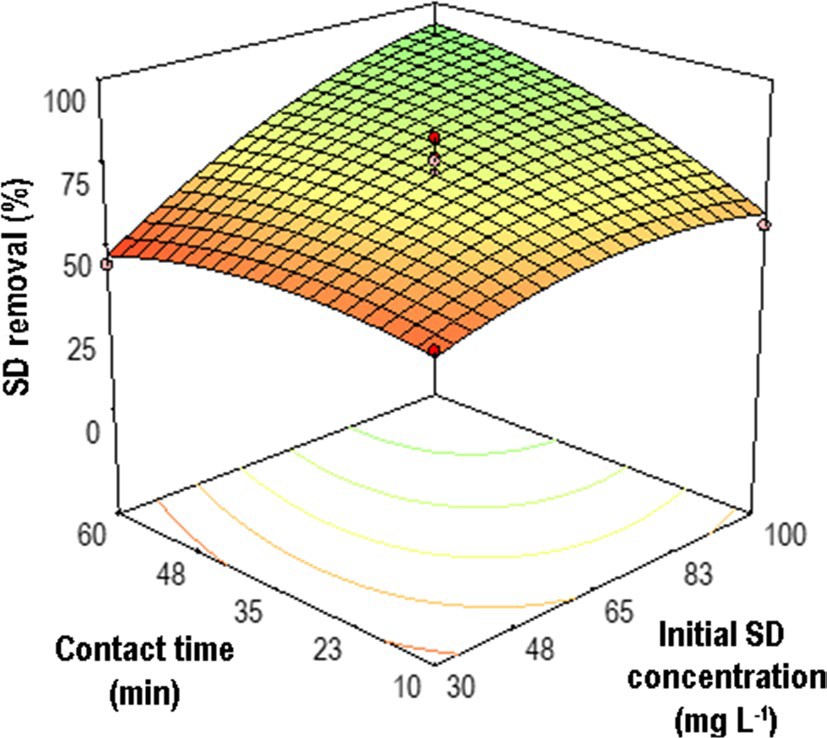
*3*

2

*X*

*4*

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Residual | 676.69 | 13 | 52.05 |  | | |
| Lack of fit | 559.67 | 10 | 55.97 | 1.43 | 0.4252 | Not significant |
| Pure error | 117.02 | 3 | 39.01 |  |  |  |
| Cor total | 8192.21 | 29 |  |  |  |  |



**Fig. 3** 3D response surface plot of the significant interaction effects of contact time and initial SD concentration on SD removal

the adsorbate pKa, both RHB and SD had negatively charged surfaces. This explains the low SD removal at higher solu- tion pH, as the increasing electrostatic repulsion reduced the adsorption of SD onto the RHB. When pH is around pKa of 4.15, the increase of negative species of SD may cause a decrease of removal efficiency. At pH = 2, most of the SD are neutral whereas the adsorbent is positively charged, thus the hydrogen bonding between SD (carbonyl oxygen) and adsor- bent (hydroxyl hydrogen) may exist. Also, at lower solution

pH, the carboxyl groups (–COOH; pKa = 1.7–4.7) formed negatively charged carboxylate groups (–COO–) (Tran et al. [2017](#_bookmark69)). These adsorbent binding sites were mainly respon- sible for the high SD removal through interaction with the positively charged SD molecules, even at pH levels below pHpzc. This can be seen from the FTIR results that show large shifts of C = O of carbonyl/carboxyl groups before and after adsorption. For comparison, pH 2 and pH 7 were used in the succeeding experiments.

Figure [4](#_bookmark8)b shows the relationship between SD removal and initial SD concentration (mg L−1) at two different solu- tion pH. As the initial SD concentration was raised from 30 to 100 mg L−1 at solution pH of 2, SD removal improved from 88% to 97%. At higher solution pH of 7, SD remov- als also improved from 61% to 77% for 30 and 100 mg L−1 SD solutions, respectively. These indicate that the SD removals are dependent on initial SD concentration. The observed high SD removal at the low initial SD concentra- tion of 30 mg L−1, especially at pH 2, can be attributed to the lower amount of SD molecules competing for sorption onto the RHB surface (Ong et al. [2018](#_bookmark60)). The improved SD removal as the initial SD concentration was raised was due to the increased interaction through collision between the SD molecules and the available binding sites on the RHB, thereby resulting in higher probability of these molecules to attach to the adsorbent (Mane et al. [2007](#_bookmark55)).

Figure [4](#_bookmark8)c shows the relationship between SD removal and RHB dosage. At solution pH of 2 and as RHB

**100**

**80**

**SD removal (%)**

**60**

**40**

**20**

**0**

**100**

**80**

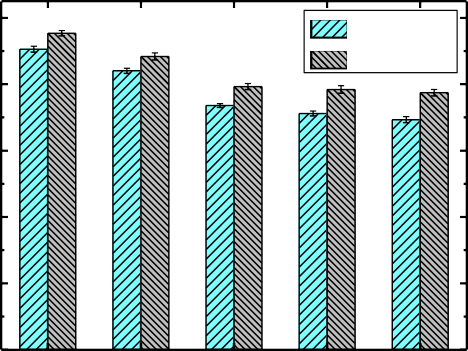
**SD removal (%)**

**60**

**40**

**20**

**2 3 4 5 7**



**(a)**

**0.1 g RHB**

**0.5 g RHB**

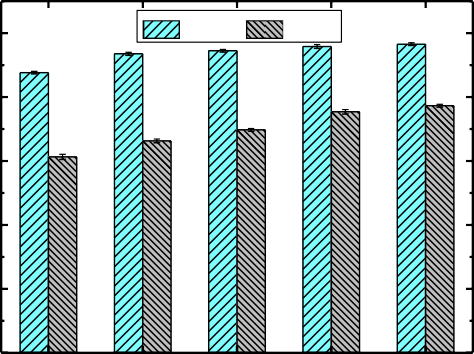
**pH**

## Adsorption isotherms

One of the most important criteria in selecting a suitable adsorbent is by studying the adsorption isotherm which provides fundamental physiochemical data for evaluat- ing the adsorption capacities of an adsorbent. The data obtained at the two pH levels were fitted using Langmuir, Freundlich, and Temkin adsorption equations.

The Langmuir isotherm model represents the equi- librium distribution of pollutant molecules between the solid and liquid phases. It is valid for monolayer adsorp- tion onto a surface containing a finite number of identical sites (Langmuir [1918](#_bookmark48)). The model assumes uniform ener- gies of adsorption onto the surface and no transmigration of adsorbate occurs in the plane of the surface. Formation of a monolayer adsorbate on the outer surface of the adsor- bent eventually reaches a saturation point where the maxi- mum adsorption of the surface is achieved and no further adsorption takes place (Boparai et al. [2011](#_bookmark21)). Langmuir isotherm model is expressed mathematically in Eq. ([4](#_bookmark6)). The values of *Qm* and *b* are computed from the slope and y-intercept of the plot of *1/Q* and *1/Ce.*

1 = 1 1 + 1 .



**(b)**

**pH 2**

**pH 7**

(4)

**0 30 40 60 80 100**

*Q bQm Ce Qm*

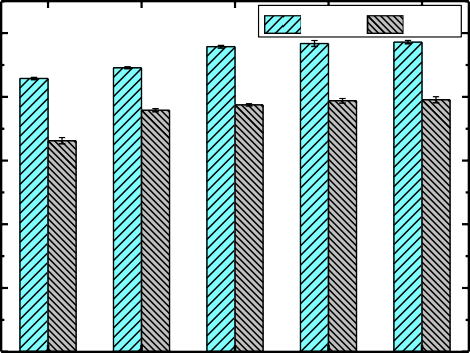
**100**

**80**

**SD removal (%)**

**60**

**40**



**(c)**

**pH 2**

**pH 7**

**Initial SD concentration (mg L-1)**

The separation factor, *RL*, also called the equilibrium parameter, is a dimensionless constant used to validate if experimental data conform to the Langmuir isotherm. The criteria for applicability to the Langmuir isotherm depends on the *RL* value as computed using Eq. ([5](#_bookmark7)) where: (*RL* = 1) follows a linear isotherm, (*RL* > 1) means an unfavorable isotherm, (*RL* < 1) corresponds to a favorable isotherm, and (*RL* = 0) is an irreversible isotherm.

*R* = 1 .

**20** *L* 1 + *bCo*

(5)

**0 0.1**

**0.2**

**0.3**

**RHB dosage (g)**

**0.4**

**0.5**

Meanwhile, the Freundlich isotherm assumes hetero- geneous surface and adsorption sites with varying energy of adsorption (Freundlich [1906](#_bookmark33)). The model assumes that the stronger binding sites on the heterogeneous surface

**Fig. 4** SD removal at varying **a** initial pH, **b** initial SD concentration, and **c** RHB dosage

dosage increased from 0.1 to 0.5 g, SD removal significantly

are initially occupied, and a decrease in binding strength occurs as the degree of site occupation is increased. The Freundlich isotherm can be expressed as follows:

1

improved from 86% to 97%. A similar trend was observed

ln *Q* = ln *Kf* + *n* ln *Ce*.

(6)

at pH 7 where a noticeable rise in SD removal (66–79%) occurred as RHB dosage was increased from 0.1 to 0.5 g. The improvement in SD removal at higher RHB dosage is attributed to the greater number of available binding sites for interaction with SD molecules (Overah [2011](#_bookmark61)).

The slope of *1/n* ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value approaches zero. A value for *1/n* below one indicates normal Langmuir isotherm.

The Temkin isotherm equation is characterized by a uniform distribution of binding energies (Temkin and Pyz- hev [1940](#_bookmark67)). The slope and intercepts are determined by

**Table 3** Isotherm parameters for SD removal using RHB Parameter Value

pH 2 pH 7

plotting the quantity adsorbed *Q* against *ln Ce* and the con-

stants and take into account the presence of indirect inter- actions between the adsorbent and adsorbate as shown in Eq. ([7](#_bookmark10)). The model assumes that heat of adsorption (func- tion of temperature) of all molecules in the layer decreases with coverage linearly rather than logarithmically.

|  |  |  |
| --- | --- | --- |
| *qm* (mg g−1) | 14.7929 | 11.8483 |
| *b* (L mg−1) | 0.1703 | 0.0052 |
| *R2* | 0.9827 | 0.9460 |
| Freundlich |  |  |
| *Kf* (mg1-1/n L1/n g-1) | 2.0943 | 0.0618 |
| *n* | 1.1148 | 0.9831 |
| *R2* | 0.9740 | 0.9258 |
| Temkin |  |  |
| *α* (L g-1) | 2.3621 | 0.1439 |

Langmuir

*Q* = *Plna* + *PlnCe*

(7)

Shown in Fig. [5](#_bookmark11) are the plots of the equilibrium adsorp- tion isotherm of diclofenac onto the RHB surface, Lang- muir, Freundlich, and Temkin isotherms for initial pH 2 and pH 7, respectively, while Table [3](#_bookmark9) shows the values for the isotherm parameters. In this study, the Langmuir isotherm gave the highest coefficient of determination for both pH 2 (*R2* = 0.9827) and pH 7 (*R2* = 0.9460). This indicates that monolayer coverage of SD onto the RHB surface, which contained homogenous and energetically equivalent sites for adsorption, is favored (Ifthikar et al. [2018](#_bookmark42)). Likewise,

*β* (J mol-1) 2.3458 2.3349

*R2* 0.8040 0.8332

no transmigration of diclofenac happened in the layer of the RHB surface (de Luna et al. [2013](#_bookmark26)). For the separation fac- tor, *RL*, the values ranged from 0.73 to 0.92 at pH 2 and 0.64

**5**



**(a)**

**pH 2**

**pH 7**

**4**

**3**

**Q**

**2**

**1**

**00 5 10 15 20 25 30 35 40**

**Ce**

**2.0**

**1.6**



**(b)**

**pH 2**

**pH 7**

**1.2**

**1/Q**

**0.8**

**0.4**

**0.0**

**0.0 0.4 0.8 1.2 1.6 2.0**

**1/Ce**

**2.0**



**(c)**

**pH 2**

**pH 7**

**1.6**

**1.2**

**0.8**

**ln Q**

**0.4**

**0.0**

**-0.4**

**-0.8**

**-1 0 1 2 3 4**

**ln Ce**

**5**

**4**



**(d)**

**pH 2**

**pH 7**

**3**

**Q**

**2**

**1**

**0**

**-1 0 1 2 3 4**

**ln Ce**

**Fig. 5 a** Adsorption isotherm of SD over RHB, **b** Langmuir, **c** Freundlich and **d** Temkin isotherm plots at pH 2 and pH 7

to 0.89 at pH 7, confirming that the isotherm is favorable at both pH levels. Thus, RHB is a suitable adsorbent for SD.

## Adsorption kinetics

Kinetic modeling was done using pseudo-first-order, pseudo-

rate-controlling step in the adsorption process. This equation indicates the fast decrease in pollutant concentration in the aqueous solution at a short time of contact suggesting an electrostatic interaction. The linearized form of the pseudo- second-order model is shown in the following equation:

*t* 1 1

second-order, and intraparticle diffusion equations for both pH 2 and pH 7 solutions to determine the dominant mecha-

= + *t*.

*qt k*2*Q*2 *Q*

(9)

nism that controls the adsorption rate, as shown in Eqs. ([8](#_bookmark13), [9](#_bookmark12), [10](#_bookmark14)). Pseudo-first-order kinetic model (Lagergren [1898](#_bookmark47)) describes the rate of pollutant removal as directly propor- tional to the pollutant concentration and assumes physisorp- tion as the rate-controlling mechanism. The integrated linear form of the pseudo-first-order model is shown in the follow- ing equation:

The intraparticle diffusion model describes the transport of the solute from the bulk of the solution onto the adsor- bent through an intraparticle process or pore diffusion. The intraparticle diffusion model demonstrating a linear relation- ship means that the pore diffusion also affects the rate of adsorption. The intraparticle diffusion model is given in the following equation:

*k*1

log *Q* − *q* = *logQ* − *t*.

(8)

*q* = *k*

*t*0.5 + *C*.

(10)

*t* 2.303

*t id*

On the other hand, the pseudo-second-order kinetic model (Ho and McKay [1998](#_bookmark39)) maintains that the rate of pol- lutant degradation is directly proportional to the square of pollutant concentration and suggests chemisorption as the

If the rate-limiting step is intraparticle diffusion, a plot of solute adsorbed against the square root of the contact time should yield a straight line passing through the origin (Oladoja et al. [2008](#_bookmark59)). However, if the y-intercept, *C*, is not equal to zero, the mechanism does not uniquely limit the

**5**



**(a)**

**pH 2**

**pH 7**

**4**

**3**

**qt**

**2**

**1**

**00 10 20 30 40 50 60**

**t**

**25**



**(c)**

**pH 2**

**pH 7**

**20**

**15**

**t/qt**

**10**

**5**

**00 10 20 30 40 50 60 70**

**t**

**0.0**

**-0.5**



**(b)**

**pH 2**

**pH 7**

**-1.0**

**log(Q-qt)**

**-1.5**

**-2.0**

**-2.5**

**-3.00 10 20 30 40 50 60 70**

**t**

**4**



**(d)**

**pH 2**

**pH 7**

**3**

**2**

**qt**

**1**

**00 1 2 3 4 5 6 7 8 9 10 t0.5**

**Fig. 6 a** Effect of contact time, **b** pseudo-first-order **c** pseudo-second-order and **d** intraparticle diffusion kinetic plots at pH 2 and pH 7

**Table 4** Kinetic parameters for SD removal by RHB Parameter Value

RHB before and after adsorption revealed that C=O stretch- ing vibrations that correspond to the carbonyl or carboxyl groups had major participation in the adsorption process.

In the adsorption study, the increase in SD concentration,

|  |  |  |
| --- | --- | --- |
|  | pH 2 | pH 7 |
| Pseudo-first order  *Q* (mg g−1) | 0.1192 | 0.5438 |
| *k*1 (min−1) | 0.0272 | 0.0887 |
| *R*2 | 0.9426 | 0.8293 |
| Pseudo-second order  *Q* (mg g−1) | 3.4317 | 2.8193 |
| *k*2 (g mg−1 min−1) | 0.8647 | 0.3393 |
| *R*2  Intraparticle diffusion  *C* (mg g−1) | 0.9999  3.3033 | 0.9998  2.511 |
| *kid* (mg g−1 min−1/2) | 0.0149 | 0.0351 |
| *R*2 | 0.9552 | 0.9651 |

contact time, and RHB dosage improved SD removal up to 97%, while the increase in the solution pH reduced SD removal. At optimum operating conditions (initial SD con- centration = 100 mg L−1, RHB dosage = 0.5 g, pH = 2), SD removal reached 96% and the calculated equilibrium adsorp- tion capacity was 3.3 mg g−1. In addition, the Langmuir iso- therm and pseudo-second order kinetics best described SD adsorption on RHB, with the highest coefficients of deter- mination at 0.9827 and 0.9999, respectively. Overall, the biochar adsorbents produced via the torrefaction of rice hulls and in the absence of activating chemicals showed excellent potential for the removal of pharmaceutical compounds such as sodium diclofenac from water matrices.

overall process, but it may be a complex combination of adsorption and intraparticle transport (Cunha et al. [2010](#_bookmark24)).

The kinetic data in Fig. [6](#_bookmark15)a revealed that the adsorp- tion process was fast during the first 10 min, and leveled off immediately afterwards when the adsorption equilib- rium was achieved. From Table [4](#_bookmark16), the pseudo-second-order model provided the best fit, and the plot of *t*/*qt* against *t* is shown in Fig. [6](#_bookmark15). This model best described the experi- mental data as shown by the high coefficients of determina- tion (*R2* = 0.9999) for both SD removals at pH 2 and pH 7. This suggests that chemisorption controlled the rate of the adsorption process (Wang et al. [2020a](#_bookmark72)). This mechanism can be described as complexation of the SD molecules with the functional groups present on the RHB, with C=O in the carbonyl or carboxyl groups having the most significant participation as indicated in the large shift of peak attrib- uted to C = O stretching vibrations observed in Fig. [2](#_bookmark1). As shown in Table [4](#_bookmark16), the adsorption capacity values (*q*pH 2 = 3.4 and *q*pH 7 = 2.8 mg g−1) determined using regression of the concentration against time were very close to the values (*q*pH 2 = 3.4 and *q*pH 7 = 2.3 mg g−1) obtained during optimi- zation. This renders the pseudo-second-order model more reliable. The value of the pseudo-second-order rate constant, *k*2, was higher at pH 2. Thus, SD molecules have high prob- ability of binding to the functional groups on the RHB at low solution pH.

# Conclusions

The RHB prepared via torrefaction was found effective in removing SD from water matrices. EDX analysis revealed that the elemental composition of the RHB adsorbent surface before and after torrefaction showed an increase in carbon atomic percentage from 25.3% to 40.48%. FTIR spectra for

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## Compliance with ethical standards

**Conflict of interest** The authors declare no competing financial inter- est.

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