Kinetic and isotherm insights of Diclofenac removal by sludge derived hydrochar

Sadish Oumabady, Paul Sebastian Selvaraj, Kalaiselvi Periasamy, Davamani Veeraswamy, Paulian Thanikanadathi Ramesh, Thava Palanisami & Sangeetha Piriya Ramasamy

Recently, hydrothermal carbonization emerges as the most viable option for the management of solid waste with high moisture content. Sludge derived hydrochar is used as an adsorbent for emerging contaminants or micro-pollutants in the domain of sustainability. Current study demonstrates the KOH activation of hydrochar produced from paper board mill sludge and evaluates its removal potential of a Non-steroidal anti-inflammatory drug, Diclofenac from aqueous solution. The activated hydrochars exhibited porous, spherical micro-structures with higher fraction of oxygenated functional groups paving way for the efficient adsorption of Diclofenac. The effect of initial Diclofenac concentration and contact time was ascertained using adsorption kinetics and isotherms. The adsorption kinetics exhibited second-order reaction for all adsorbents indicating higher coefficient of determination ($R^2 > 0.9$). The Diclofenac adsorption on hydrochars followed Langmuir isotherm model with the post-activated hydrochar recording a highest adsorption capacity of 37.23 mg g$^{-1}$ in 40 mg L$^{-1}$ initial Diclofenac concentration at 15 h equilibrium time.

In 2017, the worldwide paper production was 413 million tonnes, with India accounting for 3.18% of total paper, newsprint, and paperboard production per annum. The paper board mill industry salvages these paper products after utilization to produce recycled materials such as corrugated cardboard, wrapper and packaging boxes. The effluent treatment plants (ETP) of these industries generates semi-solid slurry from primary and secondary clarifiers known as paper board mill sludge which are managed by landfill formations and incineration. It is a heterogeneous biomass material containing very merger solid (10%) and higher moisture content (90%)$. Handling and disposal of ETP sludge is a challenging task for every industry, since it possesses many regulatory issues and requires high management cost besides environmental degradation. Hydrothermal carbonization (HTC) serves to overcome the energy-consumptive drying process for the management of organic feedstock with higher moisture content. HTC performs in relatively mild reaction temperatures between 180 and 250 $^\circ$C for 5–240 min under auto generated pressure conditions. The main advantages of HTC over other thermal processes are the use of moderate temperatures, non-requirement of inert atmosphere, kills pathogens and degrades the thermally labile pollutants. The surface modified carbon product generated from HTC known as hydrochar widens the array of its applications i.e. energy generation and storage, adsorption of contaminants and soil amendment. The hydrolysis and dehydration reactions during HTC promote the production of oxygenated functional groups thus making it an effective carbon material. Additionally, metallic concentrations of iron and calcium get concentrated and mediate the adsorption of anionic contaminants. An increase in carbon material’s cumulative surface area with a net negative charge can be achieved by improving coarseness and promoting crack development through surface modification methodologies. This will result in the enhancement of removal potential of environmental contaminants from aqueous media.

The adsorption capacity of hydrochar can be improved by activation using chemical agents. It depends on its porous nature and the kind of surface functional groups which is further influenced by the type of activation, activating agent, activation temperature and the impregnating ratio. A carbon material with high surface area is produced through KOH activation in which high temperature promotes the dissociation of KOH to form K$_2$O and further reduction to metallic K. This broadens the void between the carbonaceous layers thereby increasing the overall surface area. In addition, the pore formation on adsorbent’s surface is augmented due to the
generation of CO$_2$ during simultaneous gasification. During KOH activation, functional groups like phenolic, lactone, carbonyl, hydroxyl and carboxyl are generated. The formation of oxygenated functional groups is boosted up by the facile contact of the chemical with the carbon material’s surface thereby enhancing the micro-pores and meso-pores generation. Activation of hydrochar enhanced the porous nature of the material with the generation of large number of active sites available for the adsorption. In addition, porosity played a crucial part in improving the surface area of activated hydrochar. The activation temperature is directly proportional to the overall surface area and porosity, however, temperature more than 800 °C reduced the porosity due to the aggregation of the already prevailing pores. In a study, the effect of temperature on the porosity of KOH activated carbon materials depicted that an increase in the hydrothermal temperature beyond 280 °C directed towards a chemically stable and structurally ordered carbon. The magnitude of functional groups produced is directly proportional to the KOH to char ratio, wherein a ratio of 0.5:1 promoted enhanced adsorption potential. Activated carbon with high adsorption sites and porous nature help in removing emerging contaminants like Diclofenac from polluted environments.

Diclofenac 2-[(2,6-dichlorophenyl)amino] benzene acetic acid sodium salt, an anti-inflammatory non-steroidal drug with ubiquitous source leads to significant impacts on aquatic species as it remains biologically active and it enters into food chain. It is considered to be the most utilised non-steroidal anti-inflammatory drug (NSAID) with average consumption of 0.33 ± 0.29 g person$^{-1}$ year$^{-1}$. The NSAIDs are consumed by around 30 million people per day in average and these are excreted into the sewer system as parent chemicals or intermediates due to inadequate metabolization. These chemicals have a potential threat to the environment even at low concentration of ng L$^{-1}$ or μg L$^{-1}$. Globally, Diclofenac is consumed in huge amount (1443 ± 58 tons) per year. The maximum concentrations of Diclofenac at the global level were detected in drinking water (56 ng L$^{-1}$), surface water (57.1 μg L$^{-1}$), ground water (10.2 μg L$^{-1}$), wastewater (836 μg L$^{-1}$), soil (μg Kg$^{-1}$), sediment (309 ng g$^{-1}$), sludge (4968 μg Kg$^{-1}$), leachate (108 μg L$^{-1}$), fish (11.9 μg L$^{-1}$), mussel (4.5 μg Kg$^{-1}$) and plants (11.6 μg Kg$^{-1}$). The occurrence of 580 unique Pharmaceuticals and Personal Care Products (PPCP) in different matrices of the environment were recently screened using a downsized database of 133 studies. It was noticed that the frequency of Diclofenac was one among the top five most commonly detected PPCPs in various matrices. Furthermore, Diclofenac contributed to a 95% reduction in the vulture population in the Indian subcontinent during the 1990s owing to its renal failure and also poses serious threat to other animals, plants and aquatic organisms. A study conducted in the wastewater treatment plant sites in India reported that the total NSAIDs recorded were between 0.02 and 30 mg day$^{-1}$ per 1000 individual. Moreover, a recent research on the removal of Diclofenac using activated carbon was performed at the initial sorbate concentration of 24 to 218 mg L$^{-1}$ and reported the maximum adsorption capacity to be 180 mg g$^{-1}$. The Diclofenac removal from the aquatic environment is generally performed through conventional methods like advanced oxidation, ozonation, membrane filtration, electrochemical oxidation, ion exchange, photocatalysis and adsorption among which the latter was found to be more effective in terms of cost and removal efficiency. So, it is important to synthesize/produce low-cost adsorbent carbon materials. Most of the studies involved in the removal of Diclofenac through adsorption utilizes biodegradable non-hazardous raw material, but the present investigation attempts to utilize paper board mill sludge as a substrate for adsorbent preparation. The management of sludge is a major problem for the industries due to its hazardous nature and the cost of its disposal. With this background, the manuscript illustrates the KOH activation of hydrochar produced from paper board mill ETP sludge. Subsequently, the raw hydrochar and activated hydrochars were used for the removal of Diclofenac from synthetic aqueous solution using batch adsorption studies (Fig. 1).
Experimental methods
This study is a continued part of our earlier published research involving the production of hydrochar from paper board mill sludge and utilizing its activated forms for the removal of orthophosphate from aqueous solutions.1,25.

Hydrochar production. Effluent treatment plant of ITC Ltd., PSPD (Kovai unit), Coimbatore, India was the sample collection site for the paper board mill sludge. The samples were stored in containers at 4 °C and HTC was performed in a hydrothermal autoclave reactor at 200 °C for 10 h.1 The produced hydrochar (HC) was oven-dried to constant weight, ground and preserved for adsorption studies.

KOH pre-activation and post-activation. The main objective of performing pre- and post-activation of hydrochar is to compare the characteristic differences and their adsorption capacities. The pre-activation was performed by mixing potassium hydroxide pellets with paper board mill sludge at KOH to sludge ratio of 2:1 followed by HTC at 200 °C for 10 h. In post activation, the hydrochar was mixed with potassium hydroxide pellets at KOH to char ratio of 2:1 and the mixture was kept in tubular furnace at 600 °C for 1 h in steel tubular reactor under N2 atmosphere with heating rate of 5 °C min−1. The activated hydrochar was leached with 5 M HCl to remove excess KOH and given a wash with deionized water. The pre-activated hydrochar (PRHC) and post-activated hydrochar (POHC) were oven-dried, grounded and preserved for adsorption studies.26,27.

Hydrochar characterization. The N2 adsorption/desorption behavior of hydrochars were determined at 77 K using Belsorp mini II analyzer. The adsorbents were degassed in vacuum at 110 °C and kept overnight followed by further analysis.28 Smartsorb 92/93 surface area analyzer was used to assess the BET surface area of hydrochars. FTIR (Shimadzu’s 8400S model) was used to detect the molecular functionalities prevailing in the hydrochar at 400–4000 cm−1 wavenumber range. Horiba Scientific Nanopartica SZ-100 particle size analyzer was used to analyze the zeta potential of hydrochars.29 FEI—Quanta 250 Scanning Electron Microscope (SEM) was used to examine the structural morphologies of hydrochars at a voltage of 8 kV with ×10,000 magnification. FEI—Quanta 250 Transmission Electron Microscope (TEM) was used to interpret the hydrochar’s internal morphologies at an operating voltage 120 kV.31 The point of zero charge (pHzpc) was determined using pH drift method.

Batch adsorption studies. The batch adsorption studies were performed in 25 ml of different Diclofenac concentration (10, 20, 30, 40 and 50 mg L−1) at distinct time intervals (30, 60, 180, 360, 540, 720, 900 and 1080 min) using 0.4 g L−1 of raw (HC), Pre-activated (PRHC) and Post-activated Hydrochar (POHC) in neutral pH. Orbital shaker was used to provide continuous agitation to the experimental setup at 50 rpm. The removal efficiency and uptake per gram of adsorbents were calculated using the following Eq. (1) and (2).

\[
\text{Removal efficiency (\%) = } \left(\frac{C_0 - C_e}{C_0}\right) \times 100
\]

\[
\text{Amount of Diclofenac adsorbed by hydrochar, } Q_e (\text{mg g}^{-1}) = \left(\frac{C_0 - C_e}{m}\right) \times V
\]

where, \(C_0\) is the initial Diclofenac concentration (mg L−1), \(C_e\) is the equilibrium Diclofenac concentration (mg L−1), \(m\) is the adsorbent dry weight (g) and \(V\) is the volume of water.

Adsorption isotherms were derived for different Diclofenac concentration ranging between 10 and 50 mg L−1 at the appropriate equilibrium time in continuation to the kinetic studies. The pseudo-first-order kinetic model is stated by Eq. (3), where the amount of Diclofenac adsorbed (mg g−1) at equilibrium and at time \(t\) (min) is given by \(Q_e\) and \(Q_t\), respectively and \(k_1\) is Lagergren rate constant (min−1)32. The pseudo second order kinetic model is exhibited by the Eq. (4). Where \(k_2\) is the second order rate constant (min−1)32. The intra particle diffusion model is expressed by the Eq. (5), with an intercept \(C\) and intra particle diffusion rate constant \(k_i\) (mg g−1 h−1/2). In the elovich model Eq. (6), \(a\) is the rate of initial adsorption (mg g−1 min−1) and \(\delta\) is the surface coverage extent (g mg−1).

\[
\log(Q_e - Q_t) = \log Q_e - \frac{k_1}{2.303} t
\]

\[
\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e}
\]

\[
Q_t = k_i t^{1/2} + C
\]

\[
\frac{dQ_t}{dt} = a e^{-3Q_t}
\]
Eq. (7), where equilibrium concentration $C_e$ (mg L$^{-1}$), amount adsorbed at equilibrium $Q_e$ (mg g$^{-1}$) and Langmuir constants ($X_m$ and $K_L$) related to the adsorption efficiency and energy, respectively. The Langmuir model's assumption is that the surface adsorption takes place at homogeneous sites of POHC and the favorability of the process is confirmed by the separation factor, $R_L$ which is expressed in Eq. (8). The Freundlich isotherm postulate a non-uniform distribution of heterogeneous sites and do not assumes a monolayer adsorption capacity. It can be given by the Eq. (9), with the constants affecting the adsorption capacity $k_f$ and $n$. The log $Q_e$ versus $C_e$ plot suggests the Freundlich isotherm nature. If the value of $n$ ranges from 1 to 10, then the adsorption is considered to be feasible and good specifically, the values found more than 1 indicates its stronger adsorption force on the active sites of the hydrochars. The linear form of Temkin isotherm model is expressed by Eq. (10). The constants of Temkin isotherm i.e., equilibrium binding constant, $K_t$ (L g$^{-1}$) and constant related to heat of adsorption, $B$ (KJ mol$^{-1}$) are calculated from the intercept and slope of $Q_e$ versus $\ln C_e$ plot with the universal gas constant, $R$ (0.008314 KJ mol$^{-1}$) and the absolute temperature ($T$) in K$^{34}$.

$$
\frac{c_e}{Q_e} = \frac{1}{K_L X_m} + \frac{c_e}{X_m} \tag{7}
$$

$$
R_L = \frac{1}{1 + X_m K_L} \tag{8}
$$

$$
\log Q_e = \log k_f + \frac{1}{n} \log C_e \tag{9}
$$

$$
Q_e = \frac{RT}{B} \ln K_T + \frac{RT}{B} \ln C_e \tag{10}
$$

Diclofenac sodium$^{35}$ (Table S1) was purchased from M/s Sigma Aldrich (Merck). Type I and Type III water were used from Merck-Millipore unit for all the procedures with a resistivity of 18 MΩ cm. After each adsorption experiment, centrifugation was performed at 6000 rpm for 10 min followed by subsequent filtration. The measurement of Diclofenac was carried out at 276 nm using a Shimadzu UV-1800 UV–Vis spectrophotometer$^{36}$.  

## Results and discussion

### Hydrochar characterization

**Structural morphologies and textural characterization of hydrochars.** The color and texture of hydrochars visually varied with each other wherein the activated hydrochars depicted a dark fine texture (Fig. 2). The BET surface area were 19.59 m$^2$g$^{-1}$, 31.08 m$^2$g$^{-1}$ and 53.32 m$^2$g$^{-1}$ for HC, PRHC and POHC, respectively. The data obtained from $N_2$ adsorption/desorption were used to plot the isotherm graphs (Fig. 3). All the hydrochars (HC, PRHC and POHC) correlated with type III isotherm (convex to p/p$_0$ axis), which indicates weak adsorbent-adsorbate interactions with lower heat of adsorption than the heat of liquefaction$^{37}$. According to BET theory, the energy of monolayer adsorption is exponentially related to the parameter C. The value of “C” (intercept) in the BET plot plays a key role in deciding the type of isotherm. Although the adsorption hysteresis occurs in the reported graph, the C value in the constructed BET plot was less than 2, thereby indicating the isotherm type to be type III$^{37}$. On the surface of the adsorbent, the adsorbed molecules clusters around the most favorable sites and their amount stays finite at the saturation pressure. However, the adsorption proceeds due to greater interaction of adsorbate with an already adsorbed layer than its interaction with the adsorbent surface$^{38}$. The zeta potential of the HC was $-17.1$ mV while, it further reduced to $-20.6$ mV and $-38$ mV for PRHC and POHC, respectively. The surface charge was enhanced due to the existence of oxygenated functional groups that led to the higher adsorption capacities$^{39}$. The cation exchange capacity of the HC was $-12$ − $38$ mV for PRHC and POHC, respectively. The surface charge was enhanced due to the existence of oxygenated functional groups and cellulose, respectively. The aliphatic methyl group's vibration were represented by the band around $2800–3000$ cm$^{-1}$ with a centroid at $2920$ cm$^{-1}$ that exhibited the amino acids presence due to asymmetric C–H

**Molecular functionalities of hydrochars.** The FTIR spectra of hydrochars (Fig. 6) exhibited a variable broad OH stretching band around $3200–3600$ cm$^{-1}$ with a blunted tip at $3260$ cm$^{-1}$ due to the presence of phenolic OH groups and cellulose, respectively. The aliphatic methyl group's vibration were represented by the band around $2800–3000$ cm$^{-1}$ with a centroid at $2920$ cm$^{-1}$ that exhibited the amino acids presence due to asymmetric C–H.
stretching. The amide group formed proteins were depicted by the stretching band of C=O at 1592 cm⁻¹. The presence of –CH in the form of –CH₂ and –CH₃ was depicted by a sharp peak at 1412 cm⁻¹. The dehydration of alcohol was represented by the asymmetric stretching of C–O–C at 1026 cm⁻¹. The activation of hydrochar increased stretching of O–H, C–H, aromatic C=C, aromatic C=O and C–H bands. The OH deprotonating of activated hydrochar was noticed due to lower C–O–C vibration at 1026 cm⁻¹. The KOH activation further

Figure 2. Visual interpretation of Paper board mill ETP sludge and its derived hydrochars.

Figure 3. The N₂ adsorption/desorption isotherm.
boosted up the formation of oxygenated functional groups especially the carboxylic groups that caused the lower zeta potential values. These oxygenated functional groups influenced and further reduced the zeta potential after activation from $-17.1$ mV (HC) to $-20.6$ mV and $-38$ mV for PRHC and POHC, respectively.

Adsoption of diclofenac by hydrochars. Adsorption kinetics. The kinetic models employed for the Diclofenac adsorption by hydrochars were first-order reaction, second order reaction, Elovich model and intra particle diffusion model (Table 1). The model equations are commonly used to assess different adsorbent materials on the basis of rate constants at any given time interval. The experimental kinetic data’s goodness of fit were tested by co-efficient of determination ($R^2$). The intercept and slope value of the log ($Q_e - Q_t$) versus time plot resolved rate constant ($k_1$) for pseudo-first order kinetic model (Fig. 7a). The experimental results showed better fit for the pseudo second order kinetics. The maximum value of $R^2$ was obtained for second-order kinetics reaction in case of HC (0.9918), PRHC (0.9876) and POHC (0.9924) indicating the fitness of adsorption to second-order kinetics (Fig. 7b). The rate of adsorption was faster within 12 h of adsorption time, indicating a wide range of pores on the surface of HC, POHC, and PRHC. The process attains equilibrium when $q_t$ values reached constant value after 15 h. Diclofenac’s ionic form can be ion-exchanged with hydroxyl or carboxyl groups on the sludge or connected in the form of conjugated electron pairs. The major forces to be responsible for the adsorption of Diclofenac on the adsorbent surface include physisorption or chemisorption. Electrostatic interactions between Diclofenac and positively charged surface of HC, POHC and PRHC are the responsible driving forces for Diclofenac adsorption. In addition, interactions such as hydrophobic effects, van der Waals forces, and interactions play a role in the adsorption of Diclofenac onto hydrochar. The results obtained from the experiment revealed that the lowest adsorption capacity was found for HC (15.53 mg g$^{-1}$) than PRHC (15.95 mg g$^{-1}$) and POHC (16.63 mg g$^{-1}$). The KOH activated hydrochar exhibited higher adsorption capacity of Diclofenac due to the reasons such as higher proportion of oxygenated functional groups, higher pH$_{zpc}$ values and negative zeta potential with slightly higher surface area than pristine hydrochar. Moreover, the adsorption of Diclofenac depends on both concentration and time. The coefficient of determination of the Elovich (Fig. 7c) and intraparticle diffusion (Fig. 7d) models were lower compared to pseudo first and second order models. The results were found contradictory with the results of adsorption of pharmaceutical drugs on the adsorbents like graphene oxide and graphene, coal based activated charcoal and activated carbon. However, similar trend was reported in the removal of Diclofenac, salicylic acid and flubiprofen from KOH activated orange peel hydrochar which obeyed pseudo-second order adsorption kinetic model.

Adsorption isotherm. The adsorption capacities of different hydrochars at varying initial equilibrium concentration of Diclofenac were assessed using linear Freundlich, Langmuir and Temkin isotherm models (Table 2). The behavior of hydrochars (HC, POHC, and PRHC) showed similar trend towards Diclofenac adsorption at an equilibrium time of 15 h (Fig. 8). The isothermal adsorption curves of Diclofenac for HC ($R^2=0.932$), PRHC ($R^2=0.934$) and POHC ($R^2=0.948$) showed that the three hydrochars conformed Langmuir model, indicating the mechanism to be mono-layered (Fig. 8a). The values obtained for $R_L$ ranged from 0 to 1, indicating that the adsorption process was favorable for HC (0.96), PRHC (0.98) and POHC (0.97). The $R^2$ value of Freundlich isotherm (Fig. 8b) for HC (0.58), PRHC (0.41) and POHC (0.66) were lower than the corresponding values of Langmuir isotherm suggesting its non-applicability in the adsorption of Diclofenac. The Temkin model (Fig. 8c) became less appropriate for the Diclofenac adsorption on the hydrochars due to much lower $R^2$ values.

The adsorption capacities of POHC (37.23 mg g$^{-1}$), PRHC (36.65 mg g$^{-1}$) and HC (34.15 mg g$^{-1}$) at an initial Diclofenac concentration of 40 mg L$^{-1}$ and 15 h equilibrium period were found to be very close (Fig. 9a). At the beginning, obvious adsorption occurred within 12 h by all of the adsorbents. As the adsorption time increased further, there was an increase in adsorption capacity up to 15 h and a dip was obtained in all the adsorbents thereby indicating the equilibrium time to be 15 h. Since the adsorbents were derived from paper board mill
Figure 5. SEM and TEM micrographs of hydrochars.
sludge with moderately low carbon content and their surface area were observed to have a little difference, very close adsorption capacities were observed. The pre-activation and post-activation of hydrochars yielded significant effects on the generation of oxygenated functional groups, yet their Diclofenac adsorption capacities were not as high as some commercial activated carbon due to lower carbon content and surface area. This suggests the direct utilization of pristine sludge derived hydrochar without activation for the removal of emerging contaminants thereby confirming its cost-effectiveness. However, the removal efficiency of Diclofenac decreased gradually with corresponding increase in initial Diclofenac concentration due to the filling up of pore space.

A comparison of the present study with the related previous studies involving the adsorption of Diclofenac is illustrated in the Table S2. It can be seen that sludge derived hydrochar exhibited higher adsorption capacity towards Diclofenac than other carbon materials produced from pine bark, palm kernel shell and orange peel.

The yield of hydrochar produced from paper board mill sludge was determined in our previous study as 70%. The yield after activation decreased for the PRHC and POHC to 59% and 65%, respectively. Production and commercial practicability of hydrochar is essential in the mass production. Since HC, POHC and POHC had similar adsorption capacities, the use of HC can be a noble choice for the removal of the emerging contaminants from wastewater. The results of this investigation showed that the synthesis of hydrochar from paper board mill sludge is a simple process that does not require any pre-treatment process. Activated carbon in comparison with hydrochar production involves a very high temperature and expensive chemicals. More notably, hydrochar has reported to have a higher adsorption capacity for pharmaceuticals adsorption than other adsorbents (Table S2). Furthermore, the use of hydrochar (HC, PRHC, and POHC) to remove Diclofenac from water is a viable option under a variety of environmental conditions, including pH and high pollutant concentrations (up to 10−50 mg L−1 in this study).

|                         | HC | PRHC | POHC |
|-------------------------|----|------|------|
| **Pseudo first order**  |    |      |      |
| \( R^2 \)              | 0.9402 | 0.9577 | 0.9434 |
| \( K_1 \) (min\(^{-1}\)) | 0.0025 | 0.0025 | 0.0025 |
| **Pseudo second order** |    |      |      |
| \( R^2 \)              | 0.9918 | 0.9876 | 0.9924 |
| \( K_2 \) (g mg\(^{-1}\) min\(^{-1}\)) | 32.317 | 36.383 | 45.753 |
| **Elovich model**       |    |      |      |
| \( R^2 \)              | 0.988 | 0.98 | 0.987 |
| \( \alpha \) (mg g\(^{-1}\) min\(^{-1}\)) | 3.2522 | 2.3717 | 2.2101 |
| \( \beta \) (mg g\(^{-1}\)) | 0.2771 | 0.2856 | 0.2796 |
| **Intra particle diffusion** |    |      |      |
| \( R^2 \)              | 0.96 | 0.979 | 0.973 |
| \( K_i \) (mg g\(^{-1}\) h\(^{1/2}\)) | 0.471 | 0.451 | 0.458 |

Table 1. Kinetic parameters for Diclofenac adsorption by hydrochars.
Figure 7. Kinetics of Diclofenac removal (a) Pseudo-first order, (b) Pseudo-second order, (c) Elovich and (d) Intraparticle diffusion.

Table 2. Isotherm parameters for Diclofenac adsorption by hydrochars.
Figure 8. Isotherms of Diclofenac removal (a) Langmuir, (b) Freundlich and (c) Temkin.

Figure 9. Diclofenac removal at equilibrium time.
Conclusion
The activation of hydrochar yielded carbon micro-spheres with higher fraction of oxygenated functional groups and facilitated Diclofenac removal from aqueous solution. Hence, the risk of emerging contaminants in food chain can be controlled. This novel approach promotes simultaneous management of solid waste (sludge) and serves as water treatment option in promoting environmental sustainability. Future research will focus on the removal of emerging contaminants from natural water bodies as a scaled up study in this study area. Furthermore, new activated carbons can be produced from hydrochars for the enhancement of their adsorption capacities and development of novel applications.

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References
1. Oumabady, S. et al. Preparation and characterization of optimized hydrochar from paper board mill sludge. Sci. Rep. 10, 773 (2020).
2. Tasca, A. L. et al. Hydrothermal carbonization of sewage sludge: A critical analysis of process severity, hydrochar properties and environmental implications. Waste Manage. 93, 1–13 (2019).
3. Kim, D., Lee, K. & Park, K. Y. Hydrothermal carbonization of anaerobically digested sludge for solid fuel production and energy recovery. Fuel 130, 120–125 (2014).
4. Nakason, K. et al. Characteristics of hydrochar and liquid fraction from hydrothermal carbonization of cassava rhizome. J. Energy Inst. 91, 184–193 (2018).
5. Wang, T., Zhai, Y., Zhu, Y., Li, C. & Zeng, G. A review of the hydrothermal carbonization of biomass waste for biomass formation: Process conditions, fundamentals, and physiochemical properties. Renew. Sustain. Energy Rev. 90, 223–247 (2018).
6. Fang, J., Zhan, L., Ok, Y. S. & Gao, B. Minireview of potential applications of hydrochar derived from hydrothermal carbonization of biomass. J. Ind. Eng. Chem. 57, 15–21 (2018).
7. Jain, A., Balasubramanian, R. & Srinivasan, M. P. Hydrothermal conversion of biomass waste to activated carbon with high porosity: A review. Chem. Eng. J. 283, 789–805 (2016).
8. Spataru, A. et al. Enhanced adsorption of orthophosphate and copper onto hydrochar derived from sewage sludge by KOH activation. RSC Adv. 6, 101827–101834 (2016).
9. Upmeja, A. et al. Sustainable waste mitigation: Biotemplated nanostructured ZnO for photocatalytic water treatment: Via extraction of biofuels from hydrothermal carbonization of banana stalk. RSC Adv. 6, 92813–92823 (2016).
10. Fang, J., Gao, B., Chen, J. & Zimmerman, A. R. Hydrochars derived from plant biomass under various conditions: Characterization and potential applications and impacts. Chem. Eng. J. 267, 253–259 (2015).
11. Fernandez, M. E., Ledesma, B., Román, S., Bonelli, P. R. & Cukierman, A. L. Development and characterization of activated hydrochars from orange peels as potential adsorbents for emerging organic contaminants. Bioresour. Technol. 183, 221–228 (2015).
12. Devi, P. & Saroha, A. K. Improvement in performance of sludge-based adsorbents by controlling key parameters by activation/modification: A critical review. Crit. Rev. Environ. Sci. Technol. 46, 1704–1743 (2016).
13. Hui, T. S. & Zaini, M. A. A. Potassium hydroxide activation of activated carbon: A commentary. Carbon Lett. 16, 275–280 (2015).
14. Hunsom, M. & Autthanit, C. Minireview of potential applications of hydrochar derived from hydrothermal carbonization of biomass. J. Environ. Chem. Eng. 229, 334–343 (2013).
15. Falco, C. et al. Tailoring the porosity of chemically activated hydrothermal carbons: Influence of the precursor and hydrothermal carbonization temperature. Carbon N. Y. 62, 346–355 (2013).
16. Nuthapretechan, T., Penganisch, S. & Hunsom, M. Adsorptive desulfurization of dibenzothiophene by sewage sludge-derived activated carbon. Chem. Eng. J. 228, 263–271 (2013).
17. Thalla, A. K. & Vannarath, A. S. Occurrence and environmental risks of nonsteroidal anti-inflammatory drugs in urban wastewater in the southwest monsoon region of India. Environ. Monit. Assess. 192, 1–13 (2020).
18. Lonappan, L., Rouissi, T., Kaur Brar, S., Verma, M. & Surampalli, R. Y. An insight into the adsorption of Diclofenac on different biochars: Mechanisms, surface chemistry, and thermodynamics. Bioresour. Technol. 249, 386–394 (2018).
19. Sathishkumar, P. et al. Occurrence, interactive effects and ecological risk of Diclofenac in environmental compartments and biota: A review. Sci. Total Environ. 698, 134057 (2020).
20. Reyes, N. J. D. G., Geronimo, F. K. E., Yano, K. A. V., Guerra, H. B. & Kim, L. H. Pharmaceutical and personal care products in different matrices: Occurrence, pathways, and treatment processes. Water 13, 1159 (2021).
21. Kyas, G. Z., Fu, J., Lazaridis, N. K., Biklaris, D. N. & Matis, K. A. New approaches on the removal of pharmaceuticals from wastewater with adsorbent materials. J. Mol. Liq. 209, 87–93 (2015).
22. PraveenKumarReddy, Y. et al. Assessment of non-steroidal anti-inflammatory drugs from selected wastewater treatment plants of Southwestern India. Emerg. Contam. 7, 43–51 (2021).
23. Salvestrini, S., Fentii, A., Chianese, S., Iovino, P. & Musmarra, D. Diclofenac sorption from synthetic water: Kinetic and thermodynamic analysis. J. Environ. Chem. Eng. 8, 104105 (2020).
24. Fatemeh, F. G., Fereshteh, R. & Ahmad, D. K. A review on Diclofenac removal from aqueous solution, emphasizing on adsorption method. Iran. J. Chem. Chem. Eng. 39, 141–154 (2020).
25. Oumabady, S. et al. Application of sludge-derived KOH-activated hydrochar in the adsorptive removal of orthophosphate. RSC Adv. 11, 6535–6543 (2021).
26. Jain, A., Balasubramanian, R. & Srinivasan, M. P. Tuning hydrochar properties for enhanced mesopore development in activated carbon by hydrothermal carbonization. Microporous Mesoporous Mater. 203, 178–185 (2015).
27. Puccinelli, M., Stefanelli, E., Hiltz, M., Seggiani, M. & Vitolo, S. Activated carbon from hydrochar produced by hydrothermal carbonization of wastes. Chem. Eng. Trans. 57, 169–174 (2017).
28. Fakkaw, K., Koottatip, T. & Polprasert, C. Facel sludge treatment and utilization by hydrothermal carbonization. J. Environ. Manage. 216, 421–426 (2018).
29. Trakal, L., Bingöl, D., Pohoreč, M., Hruška, M. & Komárek, M. Geochemical and spectroscopic investigations of Cd and Pb sorption mechanisms on contrasting biochars: Engineering implications. Bioresour. Technol. 171, 442–451 (2014).
30. Kuzniatsova, T. A. et al. Synthesis of thin, oriented zeolite a membranes on a macroporous support. Adv. Funct. Mater. 18, 952–958 (2008).
31. Kliewer, C. E. Electron microscopy and imaging. In Zeolite Characterization and Catalysis 169–196 (Springer, 2009).
32. Ganasan, S. et al. Discarded biodiesel waste- derived lignocellulosic biomass as effective biosorbent for removal of sulfamethoxazole drug. Environ. Sci. Pollut. Res. https://doi.org/10.1007/s11356-019-07022-9 (2019).
33. Karthick, K., Namasiyam, C. & Pragasan, L. A. Removal of direct red 12B from aqueous medium by ZnCl2 activated jatropha husk carbon: Adsorption dynamics and equilibrium studies. Indian J. Chem. Technol. 24, 73–81 (2017).
34. Khandaker, S., Toyohara, Y., Saha, G. C., Awual, M. R. & Kuba, T. Development of synthetic zeolites from bio-slag for cesium adsorption: Kinetic, isotherm and thermodynamic studies. J. Water Process. Eng. 33, 101055 (2020).
35. Pubchem. Diclofenac sodium | C14H10Cl2NNaO2. (2018).
36. Larous, S. & Meniai, A. H. Adsorption of Diclofenac from aqueous solution using activated carbon prepared from olive stones. Int. J. Hydrog. Energy 41, 10380–10390 (2016).
37. Thommes, M. et al. Physiosorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). Pure Appl. Chem. 87, 1081–1099 (2015).
38. Danso-Boateng, E. et al. Production and characterisation of adsorbents synthesised by hydrothermal carbonisation of biomass wastes. SN Appl. Sci. 3, 1–19 (2021).
39. Sun, K., Tang, J., Gong, Y. & Zhang, H. Characterization of potassium hydroxide (KOH) modified hydrochars from different feedstocks for enhanced removal of heavy metals from water. Environ. Sci. Pollut. Res. 22, 16640–16651 (2015).
40. Maged, A. et al. New mechanistic insight into rapid adsorption of pharmaceuticals from water utilizing activated biochar. Environ. Res. 202, 111693 (2021).
41. Yan, J., Zhang, X., Lin, W., Yang, C. & Ren, Y. Adsorption behavior of Diclofenac-containing wastewater on three kinds of sewage sludge. Water Sci. Technol. 80, 717–726 (2019).
42. Saucier, C. et al. Microwave-assisted activated carbon from cocoa shell as adsorbent for removal of sodium Diclofenac and nimesulide from aqueous effluents. J. Hazard. Mater. 289, 18–27 (2015).
43. Awwand, A. M., Salem, N. M., Agarbeh, M. M. & Abdulaziz, F. M. Green synthesis, characterization of silver sulfide nanoparticles and antibacterial activity evaluation. Chem. Int. 6, 42–48 (2020).
44. Rositman, R. & Behnejad, H. A comparative adsorption study of sulfamethoxazole onto graphene and graphene oxide nanosheets through equilibrium, kinetic and thermodynamic modeling. Process Saf. Environ. Prot. 102, 20–29 (2016).
45. Caliskan, E. & Gokturk, S. Adsorption characteristics of sulfamethoxazole and metronidazole on activated carbon. Sep. Sci. Technol. 45, 244–255 (2010).
46. Moral-Rodriguez, A. I. et al. Removal of ronidazole and sulfamethoxazole from water solutions by adsorption on granular activated carbon: Equilibrium and intraparticle diffusion mechanisms. Adsorption 22, 89–103 (2016).
47. Kimbi Yaah, V. B., Zhair, M., Botelho de Oliveira, S. & Ojala, S. Hydrochar-activated carbon for removal of Diclofenac and pharmaceuticals from aqueous solutions by adsorption using a pristine polypropylene as adsorbent: Kinetic, isothermal and thermodynamic studies. Int. J. Environ. Anal. Chem. https://doi.org/10.1080/03067319.2019.1938019 (2021).
48. Cuccarese, M. et al. Removal of Diclofenac from aqueous solutions by adsorption on thermo-plasma expanded graphite. Sci. Rep. 11, 1–15 (2021).
49. Tomul, F., Arslan, Y., Bayoglu, F. T., Babucuo glu, Y. & Tran, H. N. Efficient removal of anti-inflammatory from solution by Fe-containing activated carbon: Adsorption kinetics, isotherms, and thermodynamics. J. Environ. Manage. 238, 296–306 (2019).
50. Malhotra, M., Suresh, S. & Garg, A. Tea waste derived activated carbon for the adsorption of sodium Diclofenac from aqueous solution: Adsorbent characteristics, adsorption isotherms, kinetics, and thermodynamics. Environ. Sci. Pollut. Res. 25, 32210–32220 (2018).
51. Yao, N., Huang, L. & Shuai, Q. Facile synthesis of porous carbon for the removal of diclofenac sodium from water. ACS Omega 4, 15051–15060 (2019).
52. Hiew, B. Y. Z. et al. Adsorptive removal of Diclofenac by graphene oxide: Optimization, equilibrium, kinetic and thermodynamic studies. J. Taiwan Inst. Chem. Eng. 98, 150–162 (2019).
53. Gil, A., Taoufik, N., Garcia, A. M. & Korili, S. A. Comparative removal of emerging contaminants from aqueous solution by adsorption on an activated carbon. Environ. Technol. 40, 3017–3030 (2019).
54. Wang, L. et al. A novel route for preparation of high-performance porous carbons from hydrochars by KOH activation. Colloids Surf. A 447, 183–187 (2014).
55. Romero-Anaya, A. J., Ouzzine, M., Lillo-Rodenas, M. A. & Linares-Solano, A. Spherical carbons: Synthesis, characterization and activation processes. Carbon N. Y. 68, 296–307 (2014).

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Author contributions
S.O.: Methodology, Formal analysis, Investigation, Writing—Original Draft; P.S.S.: Conceptualization, Validation, Writing—Review & Editing, Project administration; K.P.: Resources, Supervision; D.V.: Resources, Supervision; P.T.R.: Supervision, Validation; T.P.: Resources, Supervision; S.P.R.: Writing—Review & Editing.

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Correspondence and requests for materials should be addressed to P.S.S.

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