

**Adsorptive Removal of Diclofenac sodium Using Magnetic Biochar:
Relevance to Environmental Toxicology and Human Health Protection**

Dr. F. Rossi¹, Dr. M. Ibrahim¹, Dr. H. Kim¹, Dr. J. Müller², Dr. C. García², Prof. R. Thompson^{1*}

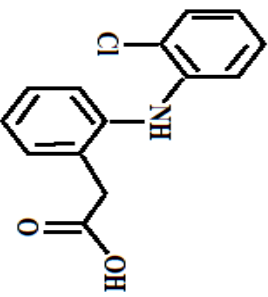
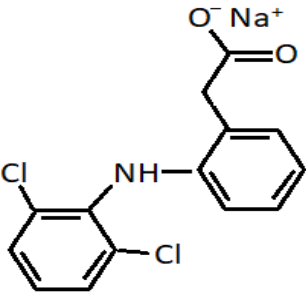
¹ School of Medicine and Population Health, University of Queensland, Brisbane, QLD 4072, Australia

² Institute of Clinical Research and Public Health, Heidelberg University, Heidelberg 69120, Germany

*Corresponding Author

1 Supplementary tables and figures

Table S1 Physicochemical properties diclofenac and its sodium salt ¹

Identity criteria	Diclofenac*	Sodium diclofenac
Chemical name (IUPAC)	2-[2-(2,6-dichloroanilino) phenyl]acetic acid	Sodium ;2-[2-(2,6-dichloroanilino) phenyl]acetate
CAS number	15307-86-5	15307-79-6
EU number	239-348-5	239-346-4
Molecular formula	C ₁₄ H ₁₁ Cl ₂ NO ₂	C ₁₄ H ₁₀ C ₁₂ NO ₂ Na
Molecular structure		
Molecular weight (g.mol ⁻¹)	296.15	318.13

Water solubility (mg.mL ⁻¹)	0.00237	0.00482
Log K _{ow}	4.15	4.26
pK _a	4.51	4.0

* Relation Molecular weight Diclofenac / Diclofenac sodium salt = 0,9309. No difference between Diclofenac / Diclofenac sodium salt was made with the effect data. A standardisation of the test results may not be needed, because of the small difference in molecular weight of both compounds.

Table S2 BET surface area and pore structure parameters of PB and PBG

Samples	BET surface area (m ² /g)	Total pore volume (cm ³ /g)	Average pore diameter (nm)
PB	222.74	0.0133	2.39
PBG	70.15	0.0586	3.34

Table S3 FTIR assignment of functional groups on each adsorbent surface

Wavenumber (cm ⁻¹)	PB	PBG	Functional group and commonly assigned component	References
3406		√	O-H bending vibrations, which show the presence of surface hydroxyl groups and physically adsorbed water	2
3433	√			
2917	√		C-H stretching vibrations in alkane or alkene groups on the surface of the carbons	3
2921		√		
2346	√	√	O-H stretch in carboxylic acid group	4
1582		√	Combination of conjugated C=O groups stretching vibration and C=C aromatic rings (lignin)	5
1579	√			
1526		√	N-H bending formation	6
1463	√		-C-H stretching from CH ₂ and CH ₃	7
1460		√		
1403		√	COO ⁻ symmetric stretching (shifted to	8

1398	√		higher wavenumber 1403)	
1095		√	C-O stretching vibration of the carboxylic acid group	5,9
1036	√			
678		√	Fe-O stretching	10
492		√		

Table S4 Parameters associated with pseudo-second-order kinetic model under the co-existing of common ions

Parameters	Co-existing metal ions					Co-existing anions				
	Ca ²⁺	Mg ²⁺	Mn ²⁺	Zn ²⁺	Fe ²⁺	Cl ⁻	NO ₃ ⁻	CO ₃ ²⁻	SO ₄ ²⁻	PO ₄ ³⁻
q _e (mg/g)	172.5	198.8	223.6	93.2	176.6	226.0	207.6	239.4	14.7	226.0
k ₂ (g/mg.min)	4.3e-4	5.1e-4	2.4e-4	1.6e-3	2.4e-4	3.5e-4	2.5e-4	1.6e-4	3.5e-3	1.1e-3
R ²	0.98	0.99	0.98	0.58	0.94	0.96	0.94	0.97	0.93	0.91

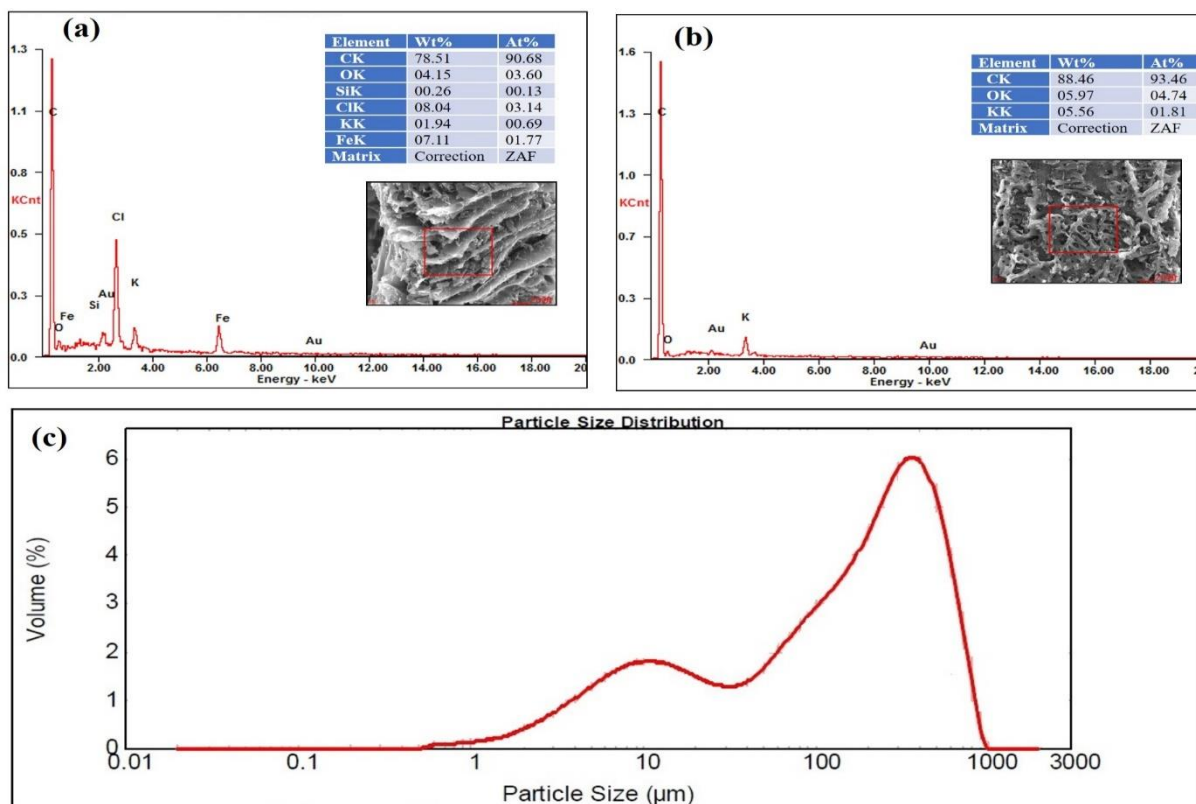


Figure S1 Energy-dispersive X-ray spectroscopy (EDS) analysis of (a) PBG and (b) PB; (c) Average particle size distribution of PBG

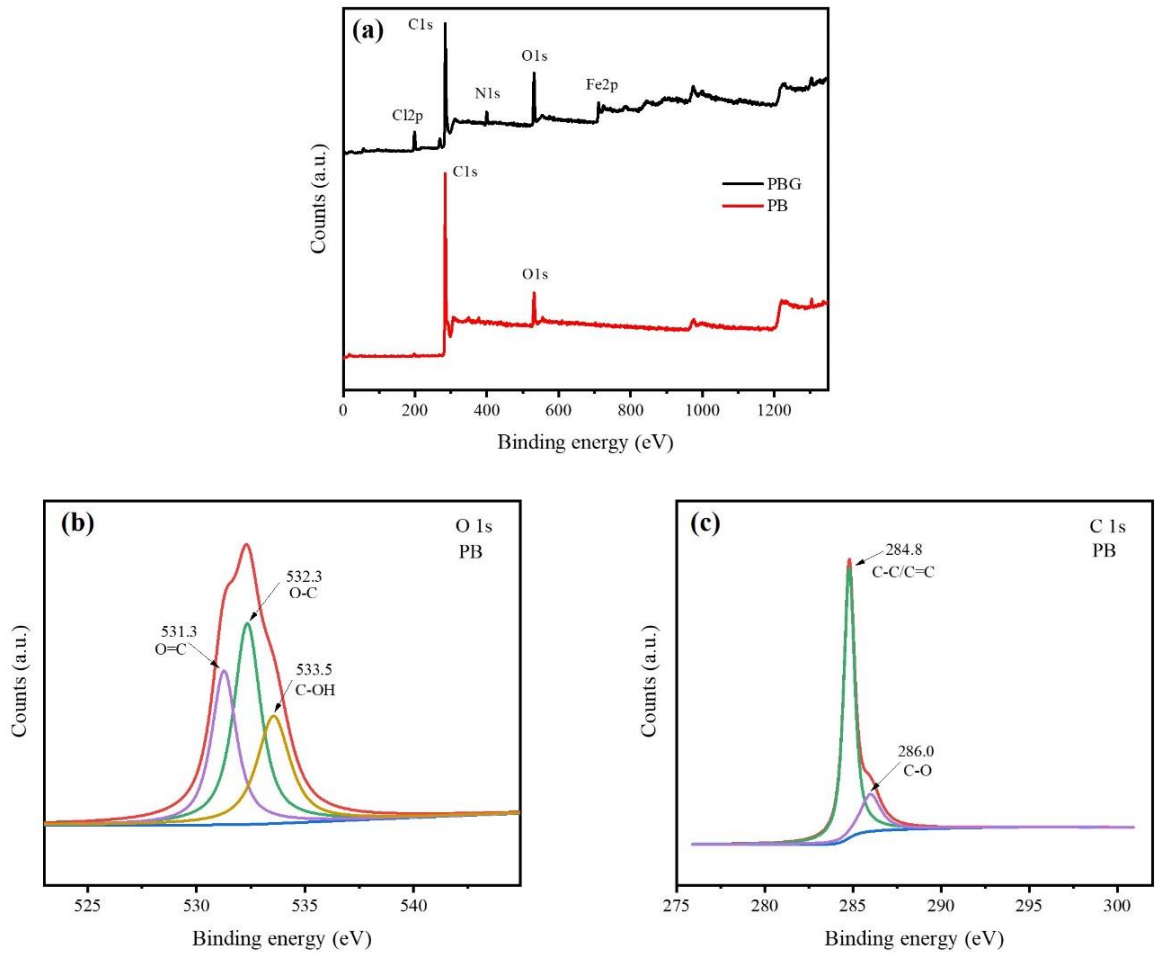


Figure S2 (a) XPS survey spectra of two sample (modified and unmodified biochar) (b) C 1s high-resolution spectra and (c) O 1s high-resolution spectra of PB sample

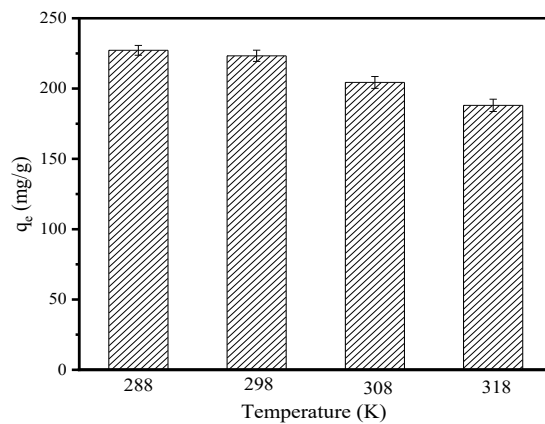


Figure S3 Effect of temperature on the DCF adsorption by PBG

2 Supplementary interpretations

2.1 Method used to calculate adsorption capacity

The concentration of sodium diclofenac (DCF) for both the initial and equilibrium solutions was determined by the ultraviolet (UV-visible) spectrophotometry method, using an equipment of Shimadzu Corporation, Japan (UV-2550). The wavelength of the highest absorbance of DCF was found at the value of 276 nm from literature researches. The conversion of the absorbance to the concentration was determined through the linear coefficient obtained from the calibration curve of sodium diclofenac. The equation is described as follows:

$$C = \frac{A}{\gamma} \quad (1)$$

Where C is the concentration of DCF solution (mg/L), A is the absorbance at 276 nm and γ is the linear coefficient of the calibration curve.

The adsorbed DCF amount was calculated by the difference between the sorption solution concentrations at initial time and equilibrium time. The adsorption capacities were obtained by the following equation:

$$q_e = \frac{(C_o - C_e)V}{W} \quad (2)$$

Where q_e (mg/g) is adsorption capacity; C_o and C_e are the initial and equilibrium concentration of DCF (mg/L), respectively; V and W are the volume of the solution (L) and adsorbents doses (g), respectively.

2.2 Models applied for the kinetic studies

There are three main steps during the adsorption process, including (1) molecular mass transfer from the solution to the adsorbent surface occurs; (2) diffusion of adsorbate to the boundary layer and (3) finally diffusion from the adsorbent surface into internal adsorbent sites via pore diffusion¹¹. The adsorption kinetic models such as pseudo-first-order, pseudo-second-order, Elovich and intraparticle diffusion model were applied to the adsorption systems.

Pseudo-first-order model

The PFO model was developed by Lagergren¹². In this model, the difference between the amount of adsorbed adsorbate on the adsorbent at equilibrium adsorption time and a defined time

are determined by the adsorption process rate. The equation used for determining adsorption process in accordance with PFO is given as follows:

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

Where, q_e and q_t are adsorbed (mg/g) DCF on the adsorbents at the equilibrium point and time t (min), respectively, and k_1 is the rate constant of adsorption (1/min).

Pseudo-second-order model

The PSO model rate equation is known as the Ho and McKay rate equation and can be written as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \quad (4)$$

Where q_e and q_t are defined similar to the parameters in the PFO model, while k_2 (g/mg/min) is the second order adsorption rate constant. Accordance with PSO model proposes that the adsorption process is governed by chemisorption.

Elovich model

The Elovich model has been widely used to describe chemical adsorption processes and suitable for systems with heterogeneous adsorbing surface. The Elovich equation is given as follows¹³:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (5)$$

Where α is the initial sorption rate (mg/g.min) and β is the desorption constant (g/mg)¹³. The constants can be obtained from the slope and intercept of a straight-line plot between q_t and $\ln(t)$.

Intraparticle diffusion model

The intraparticle diffusion model is an appropriate tool to study the diffusion mechanism of adsorbate molecules on adsorbents. Intraparticle diffusion-based mechanism proposed that uptake of DCF by adsorbents varies proportionately with the square root of contact time ($t^{1/2}$). Weber and Morris proposed this kinetic model¹⁴ and the model equation can be written as follows:

$$q_t = k_{id} t^{1/2} + C \quad (6)$$

Where q_t (mg/g) is the adsorption capacity at time t , k_{td} (mg/g.min^{1/2}) is the intraparticle diffusion rate constant and C is the intercept and represents the boundary layer thickness. The higher the C value, the higher the effect of the boundary layer.

2.3 Models applied for the isotherm studies

Langmuir isotherm model

Langmuir isotherm model was proposed by Irving Langmuir¹⁵ based on the assumption of homogeneous monolayer adsorption onto the adsorbent surface without re-adsorption of the adsorbate. The Langmuir isotherm model can be demonstrated by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max}K_L} + \frac{C_e}{q_{\max}} \quad (7)$$

Where C_e (mg/L) and q_e (mg/g) are the equilibrium concentration of the adsorbate and the amount of adsorbed adsorbate per unit mass of adsorbent at equilibrium, respectively; q_{\max} is the maximum adsorption capacity and K_L (L/mg) is Langmuir constant.

Freundlich isotherm model

The Freundlich isotherm model is often used for the description of the multilayer and heterogeneous adsorption of adsorbate onto the adsorbent surface (reference). The model equation is presented in Eq (6):

$$\ln q_e = \ln K_F + \frac{1}{n \ln C_e} \quad (8)$$

Where q_e (mg/g) and C_e (mg/L) are defined similar to Eq (5), while K_F [(mg/g)/(mg/L)^{1/n}] represents Freundlich adsorption affinity coefficient.

Temkin isotherm model

The Temkin isotherm proposes a brief interpretation on adsorbent-adsorbate interactions. In this model, the effect of adsorbate concentrations is excluded. Then it is assumed that the adsorption heat linearly decreases with the coverage of adsorbed molecules layer, and this decrease is due to the interactions between the adsorbed molecules on the surface. The equation of Temkin isotherm can be illustrated as follows:

$$q_e = \frac{RT}{b_T} \ln (k_T C_e) \quad (9)$$

Where b_T (J/mol) is the Temkin constant related to the heat of sorption, K_T (L/g) is the Temkin isotherm constant, R (8.314 J/mol. K) is the idea gas constant and T (K) is the absolute temperature.

Further, sorption energy, E (kJ/mol) can be calculated from b constant ¹⁶: $E = \frac{1}{\sqrt{2b}}$

2.4 Error functions

The fit quality and the accuracy of the parameters obtained from kinetic and isotherm studies were evaluated through determination coefficient (R^2), adjusted determination coefficient (R^2_{adj}), sum of squared errors (SEE), Chi-square test (χ^2), and average relative error (ARE), as showed in Eqs (10)-(14):

$$R^2 = 1 - \frac{\sum_i^n (q_{e,exp} - q_{e,cal})^2}{\sum_i^n (q_{e,exp} - q_{e,mean})^2} \quad (10)$$

$$R^2_{adj} = 1 - (1-R^2) \left(\frac{n-1}{n-p} \right) \quad (11)$$

$$SSE = \sum_{i=1}^n (q_{e,exp} - q_{e,cal})^2 \quad (12)$$

$$\chi^2 = \sum_{i=1}^n \frac{(q_{e,exp} - q_{e,cal})^2}{q_{e,cal}} \quad (13)$$

$$ARE = \frac{100}{n} \sum_{i=1}^n \frac{|q_{e,exp} - q_{e,cal}|_i}{q_{e,exp}} \quad (14)$$

Where $q_{e,cal}$ and $q_{e,exp}$ are respectively, the calculated and the experimental value of the equilibrium adsorbate concentration in the solid phase (mg/g), n is the number of data points.

2.5 Thermodynamic study

Thermodynamic study is conducted to investigate the temperature effect on the adsorption process. The thermodynamic parameters including standard free-energy change (ΔG^0), standard enthalpy change (ΔH^0) and standard entropy change (ΔS^0) are investigated by using the following equations:

$$\Delta G^0 = -RT \ln K^0 \quad (15)$$

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \quad (16)$$

Where R ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) is the universal gas constant, T (K) is the absolute temperature and K^0 could be calculated by plotting $\ln K_d$ ($K_d = q_e/C_e$) versus C_e and extrapolating C_e to zero. The values of ΔH^0 and ΔS^0 can be determined from the slope and intercept of the plot of ΔG^0 against T , respectively.

The ΔG^0 value indicates whether the adsorption process is spontaneous or not. If the ΔG^0 value is negative, the adsorption takes places spontaneously. Furthermore, ΔH^0 value provides the information about whether the adsorption process is endothermic or not. The adsorption process is endothermic when the ΔH^0 is a positive value.

References

- ¹DrugBank, (2020).
- ²Yue Ma, Shu-Guang Wang, Maohong Fan et al., *Journal of hazardous materials* **168**, 1140 (2009). [10.1016/j.jhazmat.2009.02.145](https://doi.org/10.1016/j.jhazmat.2009.02.145).
- ³Silvia A. Centeno and Jacob Shamir, *Journal of Molecular Structure* **873** (1), 149 (2008). <http://www.sciencedirect.com/science/article/pii/S0022286007002475>. <https://doi.org/10.1016/j.molstruc.2007.03.026>; S. Álvarez, R. S. Ribeiro, H. T. Gomes et al., *Chemical Engineering Research and Design* **95**, 229 (2015). <http://www.sciencedirect.com/science/article/pii/S026387621400478X>. <https://doi.org/10.1016/j.cherd.2014.11.001>.
- ⁴Absar Ahmad, Satyajyoti Senapati, M. Islam Khan et al., *Langmuir* **19** (8), 3550 (2003). <https://doi.org/10.1021/la026772l>. [10.1021/la026772l](https://doi.org/10.1021/la026772l).
- ⁵Juan Estrada Urbina, Alejandro Cruz-Alonso, Martha Santander-González et al., *Nanomaterials* **8**, 247 (2018). [10.3390/nano8040247](https://doi.org/10.3390/nano8040247).
- ⁶Mokgehle Letsoaloo, Taddese Godeto, Takalani Magadzu et al., *Journal of Environmental Science and Health, Part A* **54**, 1 (2019). [10.1080/10934529.2019.1609321](https://doi.org/10.1080/10934529.2019.1609321).
- ⁷Muhammad Sagir, Isa Tan, Muhammad Mushtaq et al., *Journal of Dispersion Science and Technology* **35** (2014). [10.1080/01932691.2013.859087](https://doi.org/10.1080/01932691.2013.859087).
- ⁸Guohui Long, Yuan Ji, Hongbin Pan et al., *International Journal of Food Properties* **18** (4), 763 (2015). <https://doi.org/10.1080/10942912.2014.908206>. [10.1080/10942912.2014.908206](https://doi.org/10.1080/10942912.2014.908206).
- ⁹Dongfeng Shao and Qufu Wei, *Materials* **11**, 1412 (2018). [10.3390/ma11081412](https://doi.org/10.3390/ma11081412).
- ¹⁰Lúisa Durães, Orlando Oliveira, Leandro Benedini et al., *Journal of Physics and Chemistry of Solids* **72** (6), 678 (2011). <http://www.sciencedirect.com/science/article/pii/S0022369711000539>. <https://doi.org/10.1016/j.jpccs.2011.02.020>; Asli Özge Avcı Tuna, Ercan Özdemir, Esra Bilgin Şimşek et al., *Chemical Engineering Journal* **223**, 116 (2013).

<<http://www.sciencedirect.com/science/article/pii/S1385894713002623>>.
<https://doi.org/10.1016/j.cej.2013.02.096>.

¹¹Gholam Reza Mahdavinia and Amirabbas Mosallanezhad, Journal of Water Process Engineering **10**, 143 (2016).

<<http://www.sciencedirect.com/science/article/pii/S2214714416300770>>.
<https://doi.org/10.1016/j.jwpe.2016.02.010>.

¹²S Kung %J Sven. Vetenskapsakad. Handlingar Lagergren, **24**, 1 (1898).

¹³M. J. D. Low, Chem. Rev. **60** (3), 267 (1960). <<http://dx.doi.org/10.1021/cr60205a003>>.
10.1021/cr60205a003.

¹⁴Walter J Weber and J Carrell %J Journal of the sanitary engineering division Morris, **89** (2), 31 (1963).

¹⁵Irving Langmuir, Journal of the American Chemical Society **40** (9), 1361 (1918).
<<https://doi.org/10.1021/ja02242a004>>. 10.1021/ja02242a004.

¹⁶Hong Zheng, Donghong Liu, Yan Zheng et al., Journal of Hazardous Materials **167** (1), 141 (2009). <<http://www.sciencedirect.com/science/article/pii/S0304389408019456>>.
<https://doi.org/10.1016/j.jhazmat.2008.12.093>.