Supplementary Information

Comprehensive Analysis of Cationic Dye Removal from Synthetic and Industrial Wastewater Using Semi-Natural Curcumin Grafted Biochar/Poly Acrylic Acid Composite Hydrogel

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Fig. S₁. Image of the hydrogel formation, before (left) and after (right) formation of the gel.





(b)

Fig. S₂ Possible degradation of synthesized composite hydrogel¹.



Fig. S₃ Zeta potential results of adsorbent versus pH.



Fig.S₄ Swelling of the adsorbent and pure PAA hydrogel (a), contact angle of PAA (b) and adsorbent (c).



Fig. S₅ stability analysis data with pH variation after 10 days.



Fig. S₆. Dependence of storage (G') and loss (G") modulus on the strain in strain sweep test (a) and on the angular frequency in frequency sweep test (b)



Fig. S₇ pH dependency of curcumin structure¹.



Fig. S₈ UV-Vis spectra of mixed dye solutions before and after adsorption in different pH.

		Isotherm	
Title	Linear Equation	Nonlinear Equation Parameters	
Henry's	$Q_e = K_{HE} C_e$		K_{HE} denotes the Henry's adsorption constant ² .
Langmuir	$\frac{1}{Q_e} = \frac{1}{Q_m} + \frac{1}{k_L Q_m C_e}$ $R_L = \frac{1}{1 + k_L C_i}$	$Q_e = \frac{Q}{1 + kC_e}$	k_L (L.mg ⁻¹) and Q_m (mg.g ⁻¹) signify Langmuir adsorption constant and maximum adsorption capacity at equilibrium and R_L shows the favorability of model ³ .
Freundlich	$logQ_e = \log k_f + \frac{1}{n} logC_e$	$Q_e = k_f C_e^{\frac{1}{n}}$	k_F ((mg.g ⁻¹) (L.mg) ^{1/n}) is the Freundlich constant and 1/n implies the surface heterogeneity and shows the relative distribution of energy ⁴ .
Temkin	$Q_e = \frac{RT}{b_T} lnA_T + (\frac{RT}{b_T}) lnC_e$	$Q_e = \frac{RT}{b_T} ln A_T C_e$	b_T and A_T represent Temkin models constant (KJ.mol ⁻¹) and equilibrium binding constant (L.g ⁻¹) ⁵ .
Jovanovic	$lnQ_e = lnQ_{max} - k_J C_e$	$Q_e = Q_{max}(1 - e^{kJC_e})$	k_J (L.g ⁻¹) exhibits the Jovanovic models constant and Q_{max} (mg.g ⁻¹) indicates the maximum adsorption capacity at equilibrium ⁶ .
K-C	$\frac{1}{Q_e} = \frac{1}{A_{KC}C_e^n} + \frac{B_{KC}}{A}$	$Q_e = \frac{A_{KC}C_e^n}{1 + B_{KC}C_e^n}$	A_{KC} (L ⁿ .mg ¹⁻ⁿ .g ⁻¹), B_{KC} (L.mg ⁻¹) ⁿ and n are Koble–Corrigan isotherm constants ⁷ .
Hill	$\log\left(\frac{Q_e}{Q_{SH} - Q_e}\right) = n_H \log C_e - Log k_D$	$Q_e = \left(\frac{Q_{SH}.C_e^{nH}}{K_D + C_e^{nH}}\right)$	$_{QSH}$ (mg.g ⁻¹) and k_D signify the Hill maximum uptake and isotherm constant while n_H is the cooperativity of binding interaction ⁸ .
R-P	$\ln\left(k_{R}\frac{C_{e}}{Q_{e}}-1\right) = gln(C_{e}) + ln^{\text{min}}(a_{R})$	$Q_e = \frac{k_R C_e}{1 + a_R C_e^g}$	k_R (L.g ⁻¹) and α_R (L.mg ⁻¹) are the R-P isotherm constant and g implies the models exponent ⁹ .
Sips	$\frac{1}{Q_e} = \frac{1}{Q_s k_s} (\frac{1}{C_e})^{\frac{1}{n}} + \frac{1}{Q_s}$	$Q_{e} = \frac{k_{s}Q_{s}C_{e}^{\frac{1}{n}}}{1 + k_{s}C_{e}^{\frac{1}{n}}}$	$k_{\rm S}$ (mg.L ⁻¹) and $Q_{\rm s}$ (mg.g ⁻¹) reveal the Sips adsorption isotherm constant and maximum uptake at equilibrium respectively and 1/n discloses the surface heterogeneity ¹⁰ .
		Kinetic	
PFO	$Q_t = Q_e \left(1 - exp^{-k_1 t}\right)$	$\ln\left(Q_e - Q_t\right) = \ln Q_e - k_1 t$	K_1 (min ⁻¹) implies the PFO kinetic constant and Q_e (mg.g ⁻¹) is the maximal uptake at equilibrium ¹¹ .
PSO	$Q = \frac{K_2 Q_e^2 t}{1 + K_2 Q_e t}$	$\frac{t}{Q_t} = \frac{1}{K_2 \cdot Q_e^2} + \frac{t}{Q_e}$	K_2 (g.mg ⁻¹ .min ⁻¹) shows the PSO kinetic constant and Q_e (mg.g ⁻¹) is the maximum adsorption capacity ¹² .
Elovich	$Q_t = \frac{1}{\beta} ln^{\text{initial}} (\alpha \beta \ t)$	$Q_t = \frac{1}{\beta} \ln \left(\alpha \beta \right) + \frac{1}{\beta} lnt$	α_{EI} (g.mg ⁻¹) and β_{EI} (g.mg ⁻¹) denoting preliminary rate of adsorption and Elovich model constant ¹³ .
LFD	$Q_t = Q_{\infty}[1 - exp^{\text{min}}(-Rt)]$	$\ln\left(1-\frac{Q_t}{Q_{\infty}}\right) = -R.t$	R (min ⁻¹) is fractional attainment of equilibrium and qQ_{∞} (mg.g ⁻¹) is maximum adsorption capacity at equilibrium ¹⁴ .
ID	$Q_t = k_{id}\sqrt{t}$	+ 1	K_{id} (mg/g.min ^{0.5}) indicates the intraparticle diffusion rate constant and I (mg.g ⁻¹) is a constant correlated to thickness of boundary layer ¹² .
Bangham	$Q_t = Q_m [1 - \exp\left(-k_b t^n\right)]$	$loglog\left(\frac{C_i}{C_i - Q_t M}\right) = \log\left(\frac{K_j M}{2.303 V}\right)$	Q_m and k_b signify the maximal uptake and Bangham rate coefficient, while n is the Bangham models power ¹⁵ .

Table. S_1 Linear and non-linear form of applied Isotherms and Kinetic models.



Fig. S₉ Thermodynamic plot (a), and Gibs free energy plot (b) for the adsorption of Rho and MG onto F-Biochar.



Fig. S₁₀ Graphical representation of potential adsorption phenomena during the adsorption of dye.



Fig. S₁₁ Reusability results.



Fig. S_{12} UV graph of industrial sample before and after adsorption in different pH.

Adsorbent	Adsorbate	Q_{e} (mg. g ⁻¹)	Ref
CAC MercK	MG	222.22	16
Fe ₃ O ₄ @AMCA-MIL-53 (Al)	MG	262.52	17
Sawdust carbon	MG	74.5	18
Fe ₃ O ₄ @AJPL	MG	318.3	19
PB clay	MG	497.15	20
NCH based on carrageenan, AA, and AgCl	MG	270	21
poly(AAm/AAcNa) hydrogel	Rho	469.48	22
chitosan hydrogel	Rho	556.9	23
Pyruvic acid (PA)-modified activated carbons	Rho	384.6	24
Gum ghatti and Fe ₃ O ₄ magnetic nanoparticles	Rho	654.87	3
Acrylic acid functionalized graphene oxide	Rho	437.1	25
PAA-AM/FA	Rho	366	26
CTS-g-P(AA-co-AMPS)/GO	MG	625.3	27
Biochar@curcumin/poly AA	MG	521.92	This Study
Biochar@curcumin/poly AA	Rho	742.53	

Table.S₂ Comparison with Other Literature.

References

(1) Lee, W.-H.; Loo, C.-Y.; Bebawy, M.; Luk, F.; Mason, R. S.; Rohanizadeh, R. Curcumin and its derivatives: their application in neuropharmacology and neuroscience in the 21st century. *Current neuropharmacology* **2013**, *11* (4), 338-378. DOI: 10.2174/1570159X11311040002.

(2) Ayawei, N.; Ebelegi, A. N.; Wankasi, D. Modelling and interpretation of adsorption isotherms. *Journal of chemistry* **2017**, *2017*. DOI: 10.1155/2017/3039817.

(3) Mittal, H.; Mishra, S. B. Gum ghatti and Fe(3)O(4) magnetic nanoparticles based nanocomposites for the effective adsorption of rhodamine B. *Carbohydr Polym* **2014**, *101*, 1255-1264. DOI: 10.1016/j.carbpol.2013.09.045 From NLM Medline.

(4) Kumar, N.; Reddy, L.; Parashar, V.; Ngila, J. C. Controlled synthesis of microsheets of ZnAl layered double hydroxides hexagonal nanoplates for efficient removal of Cr (VI) ions and anionic dye from water. *Journal of environmental chemical engineering* **2017**, *5* (2), 1718-1731.

(5) Ringot, D.; Lerzy, B.; Chaplain, K.; Bonhoure, J.-P.; Auclair, E.; Larondelle, Y. In vitro biosorption of ochratoxin A on the yeast industry by-products: Comparison of isotherm models. *Bioresource technology* **2007**, *98* (9), 1812-1821.

(6) Saadi, R.; Saadi, Z.; Fazaeli, R.; Fard, N. E. Monolayer and multilayer adsorption isotherm models for sorption from aqueous media. *Korean Journal of Chemical Engineering* **2015**, *32*, 787-799.

(7) Koble, R. A.; Corrigan, T. E. Adsorption isotherms for pure hydrocarbons. *Industrial & Engineering Chemistry* **1952**, *44* (2), 383-387. DOI: 10.1021/ie50506a049.

(8) Sharma, Y. Fast removal of malachite green by adsorption on rice husk activated carbon. *The Open Environmental Pollution & Toxicology Journal* **2009**, *1* (1).

(9) Ng, J.; Cheung, W.; McKay, G. Equilibrium studies of the sorption of Cu (II) ions onto chitosan. *Journal of colloid and interface science* **2002**, *255* (1), 64-74.

(10) Kumara, N.; Hamdan, N.; Petra, M. I.; Tennakoon, K. U.; Ekanayake, P. Equilibrium isotherm studies of adsorption of pigments extracted from Kuduk-kuduk (Melastoma malabathricum L.) pulp onto TiO2 nanoparticles. *Journal of Chemistry* **2014**, *2014*.

(11) Hashem, A.; Hammad, H. A.; Al-Anwar, A. Modified Camelorum tree particles as a new adsorbent for adsorption of Hg (II) from aqueous solutions: kinetics, thermodynamics and non-linear isotherms. *Desalination and Water Treatment* **2016**, *57* (50), 23827-23843.

(12) Villarante, N. R.; Bautista, A. P. R.; Sumalapao, D. E. P. Batch adsorption study and kinetic profile of Cr (VI) using lumbang (Aleurites moluccana)-derived activated carbon-chitosan composite crosslinked with epichlorohydrin. *Orient. J. Chem* **2017**, *33* (3), 1111-1119.

(13) Yousef, N.; Farouq, R.; Hazzaa, R. Adsorption kinetics and isotherms for the removal of nickel ions from aqueous solutions by an ion-exchange resin: application of two and three parameter isotherm models. *Desalination and Water Treatment* **2016**, *57* (46), 21925-21938. DOI: 10.1080/19443994.2015.1132474.

(14) Boyd, G.; Adamson, A. W.; Myers Jr, L. The exchange adsorption of ions from aqueous solutions by organic zeolites. II. Kinetics1. *Journal of the American Chemical Society* **1947**, *69* (11), 2836-2848.
(15) Hashem, A.; Badawy, S.; Farag, S.; Mohamed, L.; Fletcher, A.; Taha, G. Non-linear adsorption characteristics of modified pine wood sawdust optimised for adsorption of Cd (II) from aqueous systems. *Journal of Environmental Chemical Engineering* **2020**, *8* (4), 103966.

(16) Malik, R.; Ramteke, D. S.; Wate, S. R. Adsorption of malachite green on groundnut shell waste based powdered activated carbon. *Waste Manag* **2007**, *27* (9), 1129-1138. DOI:

10.1016/j.wasman.2006.06.009 From NLM Medline.

(17) Alqadami, A. A.; Naushad, M.; Alothman, Z. A.; Ahamad, T. Adsorptive performance of MOF nanocomposite for methylene blue and malachite green dyes: Kinetics, isotherm and mechanism. *J Environ Manage* 2018, *223*, 29-36. DOI: 10.1016/j.jenvman.2018.05.090 From NLM Medline.
(18) Garg, V. K.; Gupta, R.; Bala Yadav, A.; Kumar, R. Dye removal from aqueous solution by adsorption on treated sawdust. *Bioresour Technol* 2003, *89* (2), 121-124. DOI: 10.1016/s0960-8524(03)00058-0 From NLM Medline.

(19) Alorabi, A. Q. Effective removal of malachite green from aqueous solutions using magnetic nanocomposite: synthesis, characterization, and equilibrium study. *Adsorption Science & Technology* **2021**, *2021*, 1-15. DOI: 10.1155/2021/2359110.

(20) Mittal, H.; Parashar, V.; Mishra, S.; Mishra, A. Fe3O4 MNPs and gum xanthan based hydrogels nanocomposites for the efficient capture of malachite green from aqueous solution. *Chemical Engineering Journal* **2014**, *255*, 471-482.

(21) Dargahi, M.; Ghasemzadeh, H.; Bakhtiary, A. Highly efficient absorption of cationic dyes by nano composite hydrogels based on kappa-carrageenan and nano silver chloride. *Carbohydr Polym* **2018**, *181*, 587-595. DOI: 10.1016/j.carbpol.2017.11.108 From NLM PubMed-not-MEDLINE.

(22) Ismail, L. F.; Maziad, N. A.; Abo-Farha, S. A. Factors affecting the adsorption of cationic dyes on polymeric hydrogels prepared by gamma irradiation. *Polymer international* **2005**, *54* (1), 58-64.

(23) Tang, Y.; He, T.; Liu, Y.; Zhou, B.; Yang, R.; Zhu, L. Sorption behavior of methylene blue and rhodamine B mixed dyes onto chitosan graft poly (acrylic acid-co-2-acrylamide-2-methyl propane sulfonic acid) hydrogel. *Advances in Polymer Technology* **2018**, *37* (7), 2568-2578.

(24) Huang, Y.; Zheng, X.; Feng, S.; Guo, Z.; Liang, S. Enhancement of rhodamine B removal by modifying activated carbon developed from Lythrum salicaria L. with pyruvic acid. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2016**, *489*, 154-162.

(25) Wang, G.; Li, G.; Huan, Y.; Hao, C.; Chen, W. Acrylic acid functionalized graphene oxide: Highefficient removal of cationic dyes from wastewater and exploration on adsorption mechanism. *Chemosphere* **2020**, *261*, 127736. DOI: 10.1016/j.chemosphere.2020.127736 From NLM Medline. (26) Zhu, W.; Zhang, Y.; Wang, P.; Yang, Z.; Yasin, A.; Zhang, L. Preparation and Applications of Salt-Resistant Superabsorbent Poly (Acrylic Acid-Acrylamide/Fly Ash) Composite. *Materials (Basel)* 2019, *12*(4), 596. DOI: 10.3390/ma12040596 From NLM PubMed-not-MEDLINE.

(27) Zhu, L.; Liu, Y.; Yaoji Tang, Y. L. Synthesis of chitosan graft poly (acrylic acid-co-2-acrylamide-2methylpropanesulfonic acid)/graphite oxide composite hydrogel and the study of its adsorption. *Polymers and Polymer Composites* **2022**, *30*, 09673911221086164.