

Supporting Information

Sustainable Hydrochar from Orange Peel and Bagasse: A Wet Pyrolysis Approach for Efficient Fe²⁺ and Mn²⁺ Removal from Water Using a Factorial Design

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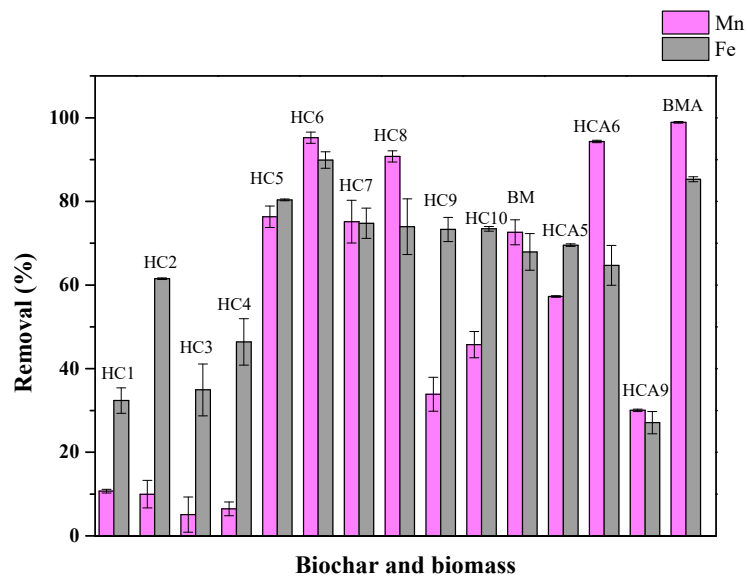


Figure S1. Efficiency of biochar in the removal of Fe^{2+} and Mn^{2+} .

Conditions: $[\text{Fe}^{2+}]$ or $[\text{Mn}^{2+}] = 10 \text{ mg L}^{-1}$; solution volume = 20 mL; biochar mass = 50 mg, time = 24 h, Temperature = $\sim 25^\circ\text{C}$. Caption: HC1 (200 $^\circ\text{C}$; 14 h; H_3PO_4); HC2 (200 $^\circ\text{C}$; 14 h; NaOH); HC3 (200 $^\circ\text{C}$; 8 h; H_3PO_4); HC4 (200 $^\circ\text{C}$; 8 h; NaOH); HC5 (100 $^\circ\text{C}$; 14 h; H_3PO_4); HC6 (100 $^\circ\text{C}$; 14h; NaOH); HC7 (100 $^\circ\text{C}$; 8h; H_3PO_4); HC8 (100 $^\circ\text{C}$; 8h; NaOH); HC9-HC10 (150 $^\circ\text{C}$; 11 h, without activation agent); HCA5 (BC05 thermally activated, 300 $^\circ\text{C}$, 1 h); HCA6 (BC06 thermally activated, 300 $^\circ\text{C}$, 1 h); HCA9 (BC09 thermally activated, 300 $^\circ\text{C}$, 1 h) e BMA (biomass thermally activated, 300 $^\circ\text{C}$, 1 h)

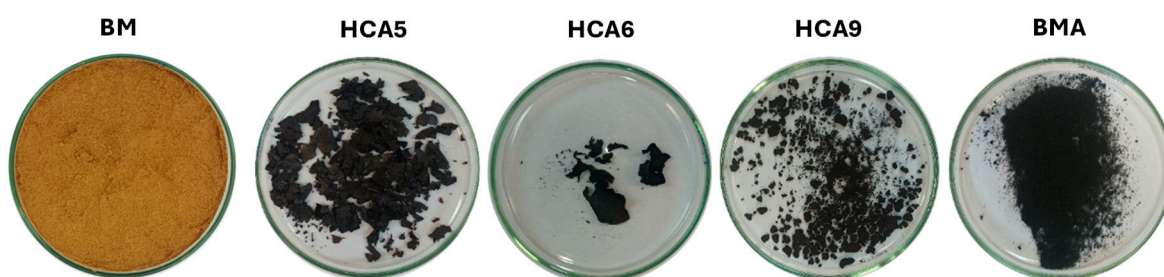


Figure S2. Thermally activated biochars (1h, 300 $^\circ\text{C}$).

Caption: BM: Biomass (orange peel and pulp) HCA5 (Precursor HC5: 100 $^\circ\text{C}$; 4 h; H_3PO_4); HCA6 (HC6: 100 $^\circ\text{C}$; 14 h; NaOH); HCA9 (HC9: 150 $^\circ\text{C}$; 11 h, without activating agent) and BMA (biomass).

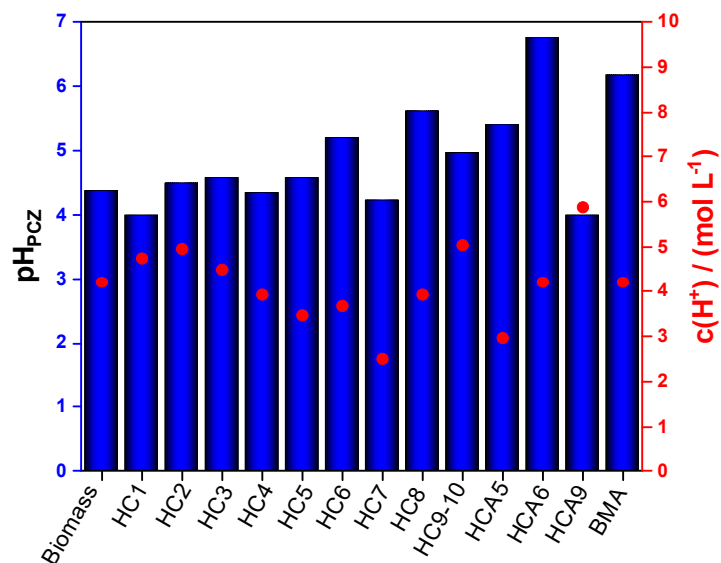


Figure S3. pH_{PZC} and Brønsted acid concentration for different biochars.

Caption: HC1 (200 °C; 14 h; H₃PO₄); HC2 (200 °C; 14 h; NaOH); HC3 (200 °C; 8 h; H₃PO₄); HC4 (200 °C; 8 h; NaOH); HC5 (100 °C; 14 h; H₃PO₄); HC6 (100 °C; 14 h; NaOH); HC7 (100 °C; 8 h; H₃PO₄); HC8 (100 °C; 8 h; NaOH); HC9-HC10 (150 °C; 11 h, without activating agents); HCA5 (BC05 thermal activation, 300 °C, 1 h); HCA6 (BC06 thermal activation, 300 °C, 1 h); HCA9 (HC9 thermal activation, 300 °C, 1 h) e BMA (biomass thermal activation, 300 °C, 1 h).

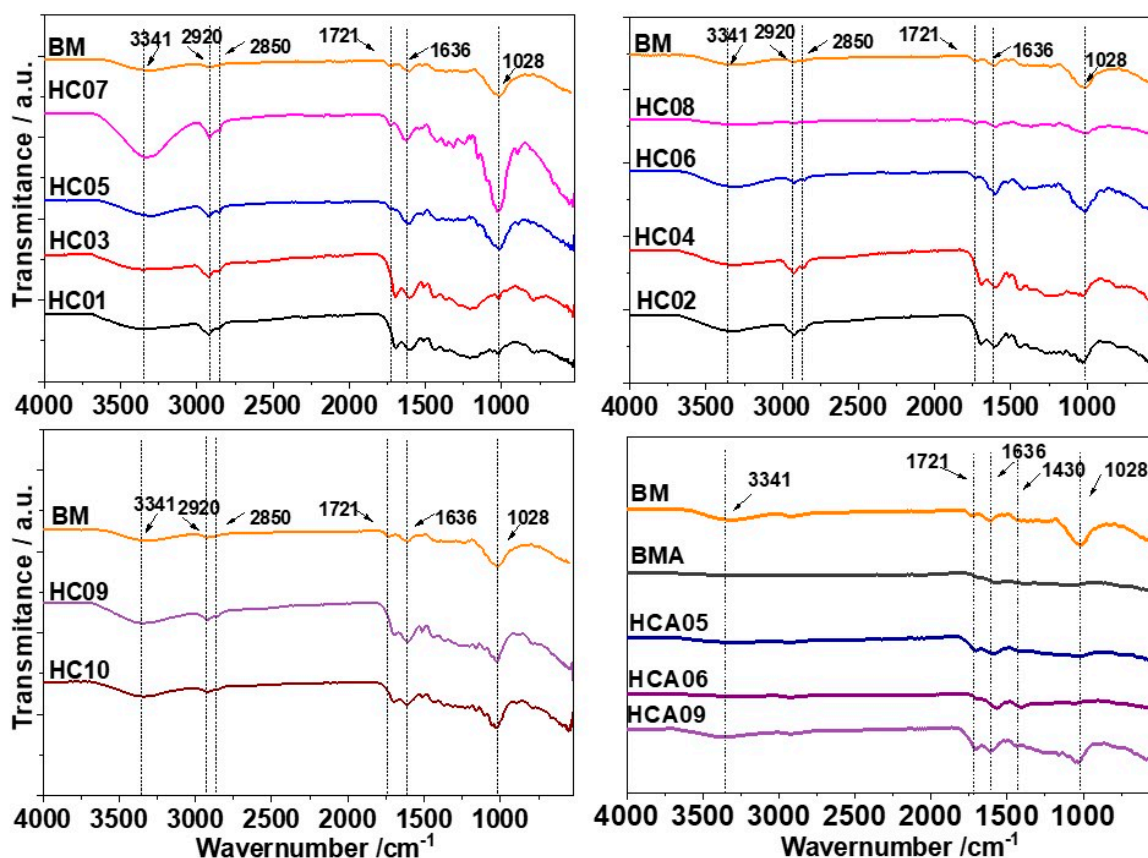


Figure S4. Fourier transform infrared (FTIR) spectrum of biochars (a) activated with H_3PO_4 , (b) NaOH , (c) without activating agent (water) and (d) thermally activated. Caption: HC1 (200 °C; 14 h; H_3PO_4); HC2 (200 °C; 14 h; NaOH); HC3 (200 °C; 8 h; H_3PO_4); HC4 (200 °C; 8 h; NaOH); HC5 (100 °C; 14 h; H_3PO_4); HC6 (100 °C; 14h; NaOH); HC7 (100 °C; 8 h; H_3PO_4); HC8 (100 °C; 8 h; NaOH); HC9-HC10 (150 °C; 11 h, without activating agents); HCA5 (BC05 thermal activation, 300 °C, 1 h); HCA6 (BC06 thermal activation, 300 °C, 1 h); HCA9 (HC9 thermal activation, 300 °C, 1 h) e BMA (biomass thermal activation, 300 °C, 1 h).

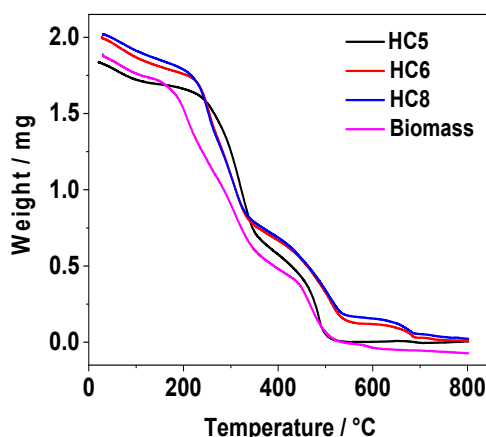


Figure S5. Thermogravimetric analysis (TGA) for HC5, HC6, HC8, and biomass. Captions: HC5 (100 °C; 14 h; H_3PO_4); HC6 (100 °C; 14h; NaOH); HC8 (100 °C; 8h; NaOH); HCA6 (HC6 thermally activated, 300 °C, 1 h) and BMA (biomass thermally activated, 300 °C, 1 h).

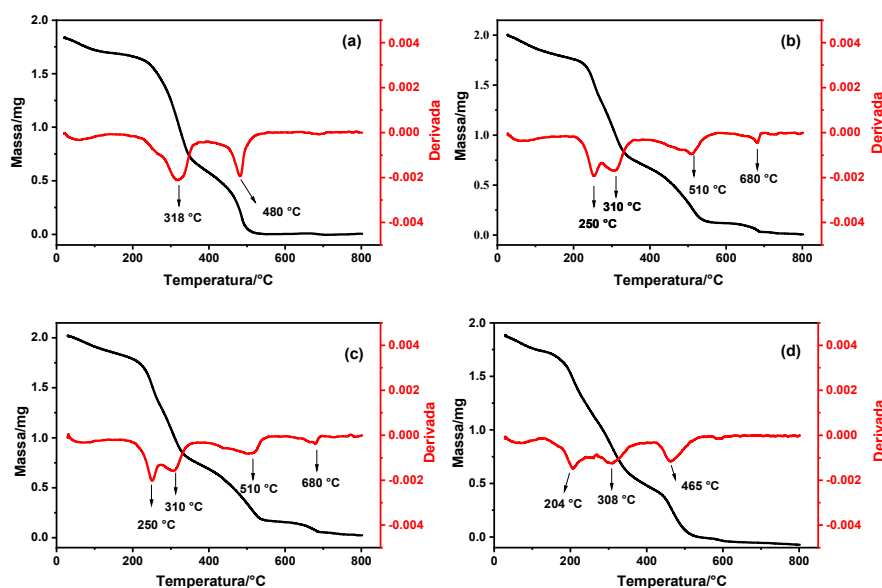


Figure S6. TGA/DTG (a) HC5 (b) HC6 (c) HC8 e (d) biomass.
 Legende: HC5 (100 °C/ 14 h/ H₃PO₄); HC6 (100 °C/ 14 h/ NaOH); HC8 (100°C/ 8 h/ NaOH)

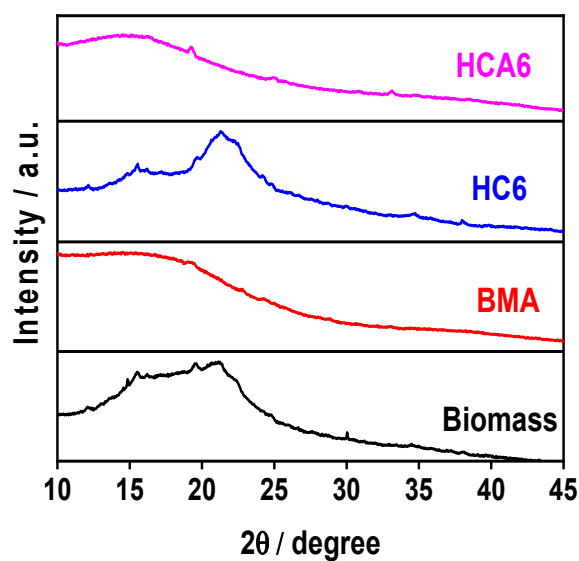


Figure S7. X-ray diffraction patterns of the hydrochar (HC6) and biomass, and both thermally activated (HCA6 and BMA). Captions: HC5 (100 °C;14 h; H₃PO₄); HC6 (100°C; 14h; NaOH); HC8 (100°C; 8h; NaOH); HCA6 (HC6 thermally activated, 300 °C, 1 h) and BMA (biomass thermally activated, 300 °C, 1 h).

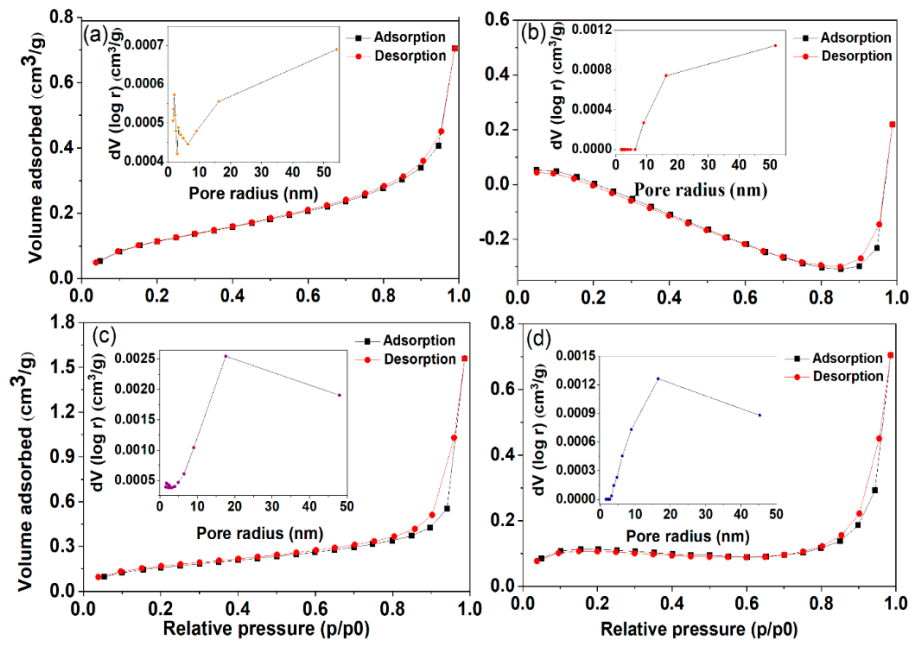


Figure S8. Isotherms of N₂ adsorption/desorption for the hydrochars (a) BM, (b) BMA, (c) HC6, and (d) HCA6. Captions: HC6 (100 °C; 14h; NaOH); HCA6 (HC6 thermally activated, 300 °C, 1 h); BM (biomass) and BMA (biomass thermally activated, 300 °C, 1 h).

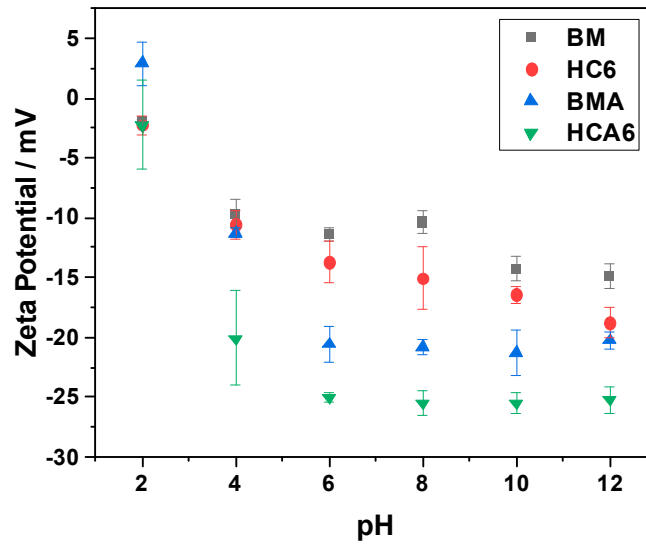


Figure S9. Zeta Potential for biomass, biochar, and both thermally activated. Legend: BM (biomass), BMA (biomass thermal activation, 300 °C, 1 h), HC6- Biochar (100 °C/ 14 h/ NaOH) e HCA6 - (Biochar thermal activation, 300 °C, 1 h).

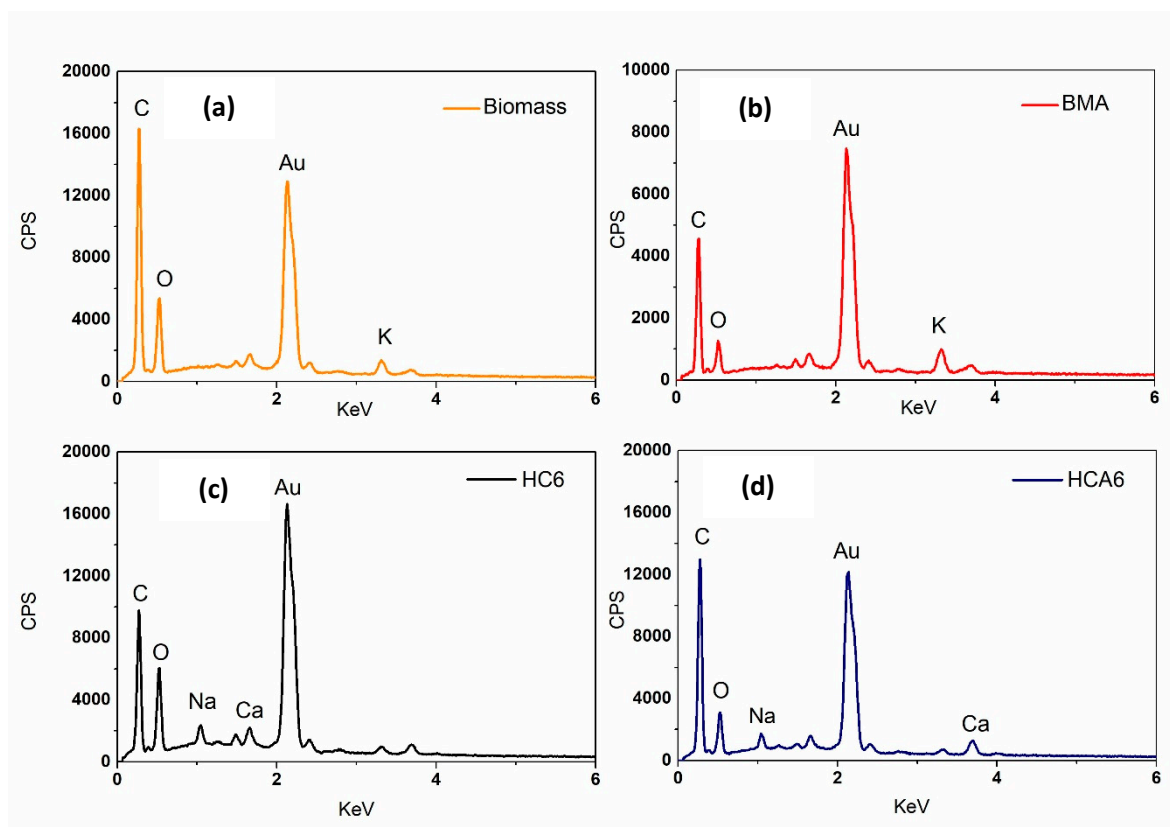


Figure S10. Energy Dispersive Spectroscopy (EDS) spectra for the samples (a) biomass, (b) BMA(Biomass thermal activation, 300 °C, 1 h), (c) HC6 (100 °C; 14 h; NaOH) and (d) HCA6 (HC6 thermal activation, 300 °C, 1 h).

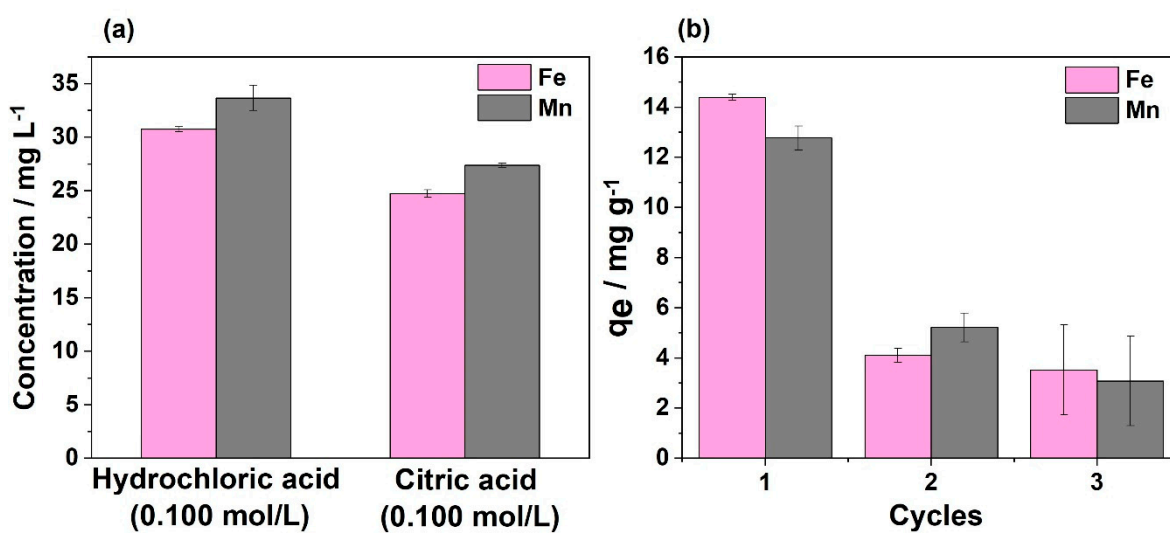


Figure S11. (A) Removal efficiency of iron (Fe) and manganese (Mn) using different extracting solutions and (B) Reuse of HC6 in different adsorption cycles.

Table S1. Statistical Analysis for the 2³ Factorial Design to Evaluate Which Biochar Synthesis Variables Influenced Manganese and Iron Removal.

		Effect	Error	t(13)	p	Coefficient	Error
Mn ²⁺	T	-76.3004	2.682708	-28.4416	0.000000	-38.1502	1.341354
	t	3.6890	2.682708	1.3751	0.192340	1.8445	1.341354
	AA	-8.7845	2.682708	-3.2745	0.006037	-4.3923	1.341354
	T×t	0.8758	2.682708	0.3265	0.749273	0.4379	1.341354
	T×AA	8.4660	2.682708	3.1558	0.007587	4.2330	1.341354
	t×AA	-0.2919	2.682708	-0.1088	0.915007	-0.1460	1.341354
Fe ²⁺	T	-35.9430	3.372806	-10.6567	0.000000	-17.9715	1.686403
	t	8.5201	3.372806	2.5261	0.025311	4.2600	1.686403
	AA	-12.3277	3.372806	-3.6550	0.002909	-6.1639	1.686403
	T×t	-2.2360	3.372806	-0.6629	0.518950	-1.1180	1.686403
	T×AA	-7.9702	3.372806	-2.3631	0.034378	-3.9851	1.686403
	t×AA	-7.0035	3.372806	-2.0765	0.058245	-3.5018	1.686403

T = temperature, t = time, AA = activation agent

Table S2. Analysis of Variance

	Factor	Sum of squares	Degrees of freedom	Mean square	F-statistic	p-value
Mn ²⁺	(1)Temperature	23287.02	1	23287.02	808.92	0.000000
	(2)Time	54.43	1	54.43	1.8909	0.192340
	(3)AA	308.67	1	308.67	10.7223	0.006037
	1 by 2 (T×t)	3.07	1	3.07	0.1066	0.749273
	1 by 3 (T×AA)	286.69	1	286.69	9.9589	0.007587
	2 by 3 (t×AA)	0.34	1	0.34	0.0118	0.915007
	Error	374.24	13	28.79		
	Total SS	24314.47	19			
Fe ²⁺	(1)Temperature	5167.59	1	5167.59	113.56	0.000000
	(2)Time	290.36	1	290.36	6.3812	0.025311
	(3)AA	607.89	1	607.89	13.36	0.002909
	1 by 2 (T×t)	19.99	1	19.99	0.44	0.518950
	1 by 3 (T×AA)	254.09	1	254.09	5.58	0.034378
	2 by 3 (t×AA)	196.19	1	196.19	4.31	0.058245
	Error	591.543	13	45.503		
	Total SS	7127.679	19			

Table S3. Physicochemical characterization of biochars obtained from bagasse and orange peel biomass using a 2³ factorial design, through hydrothermal carbonization and thermal activation processes.

MATERIAL	YIELD (%)	C (%)	H (%)	N (%)	S (%)	O ^a (%)	H/C	O/C	pH _{PZC}	c(H ⁺) (mmol g ⁻¹)
BM	---	41.26	6.49	1.00	2.36	48.87	1.88	0.889	4.39	4.2±0.1
HC1	39	68.17	4.75	1.28	2.55	23.22	0.83	0.255	4.00	4.8±0.4
HC2	35	64.80	5.72	1.59	3.31	24.55	1.05	0.284	4.50	5.0±0.6
HC3	40	69.80	4.80	1.29	2.76	21.33	0.82	0.229	4.59	4.5±0.3
HC4	32	68.26	6.54	1.75	2.66	20.77	1.14	0.228	4.35	4.0±0.3
HC5	19	57.75	4.56	1.36	2.99	33.32	0.94	0.433	4.58	3.5±0.6
HC6	39	42.65	6.04	1.26	1.95	48.06	1.69	0.845	5.20	3.7±0.1
HC7	17	44.87	5.79	1.15	0.66	37.22	1.54	0.622	4.23	2.5±0.5
HC8	42	29.36	4.19	0.71	1.15	64.56	1.70	1.650	5.61	4.0±0.5
HC9-10	43±8	59.3±0.9	5.4±0.5	1.41±0.05	2.3±0.2	31.7±0.7	1.3±0.4	0.401±0.01	5.0±0.9	5.0±0.4
HCA5	14	54.73	4.92	1.81	1.66	36.86	1.07	0.505	5.40	3.0±0.1
HCA6	19	62.48	5.15	1.95	1.43	28.97	0.98	0.348	6.76	4.2±0.1
HCA9	31	56.74	3.34	1.49	1.36	37.04	0.70	0.490	4.00	5.9±0.3
BMA	38	61.01	3.60	2.33	2.68	30.36	0.70	0.373	6.17	4.2±0.4

Caption: HC1 (200 °C; 14 h; H₃PO₄); HC2 (200 °C; 14 h; NaOH); HC3 (200 °C; 8 h; H₃PO₄); HC4 (200 °C; 8 h; NaOH); HC5 (100 °C; 14 h; H₃PO₄); HC6 (100 °C; 14 h; NaOH); HC7 (100 °C; 8 h; H₃PO₄); HC8 (100 °C; 8 h; NaOH); HC9-HC10 (150 °C; 11 h, without activating agents); HCA5 (BC05 thermal activation, 300 °C, 1 h); HCA6 (BC06 thermal activation, 300 °C, 1 h); HCA9 (HC9 thermal activation, 300 °C, 1 h) e BMA (biomass thermal activation, 300 °C, 1 h). ^aCalculated by the difference: % O = 100 % - (% C + % N + % H + % S) - % Ash.

Table S4. Textural Characteristics of Biomass and Biochars Obtained from Orange Peel Before and After Thermal Activation.

Sample	Surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore radius (nm)
BM	0.2903	0.00100	1.533
HC6	0.5990	0.00150	N.A.
HCA6	0.1313	0.00105	8.908
BMA	0.0619	0.00088	16.278

Caption: BM (biomass), BMA (thermally activated biomass, 300 °C, 1 h), HC6 - Biochar (100°C / 14 h / NaOH), and HCA6 - (Thermally activated biochar, 300 °C, 1 h). N.A. Not determined.

Table S5. Elemental Composition Determined by Energy Dispersive X-ray Spectroscopy (EDS)

Element	Content/%			
	Biomass	BMA	HC6	HCA6
C	60.54	69.53	50.03	64.28
O	34.44	25.51	40.67	26.15
K	3.51	3.65	2.19	1.50
Ca	1.50	1.31	3.58	5.18
Na	-	-	3.53	2.49
Mg	-	-	-	0.40

Table S6. Immediate Analysis for Biomass, Biochar 06, and Both Thermally Activated.

Sample	Moisture (%)	Volatile (%)	Ash (%)	Fixed carbon (%)
BM	10.2	87.3	3.5	9.2
BMA	5.0	57.2	13.2	29.5
HC6	6.1	92.0	5.4	2.6
HCA6	4.6	42.7	18.2	39.2

Caption: BM (biomass), BMA (thermally activated biomass, 300 °C, 1 h), HC6 - Biochar (100°C / 14 h / NaOH), and HCA6 - (Thermally activated biochar, 300 °C, 1 h).

Table S7. Kinetic parameters of Fe²⁺ and Mn²⁺ adsorption by biochar HC6

Model	Parameter	Fe	Mn
Pseudo-first-order (PPO)	q _e ¹ , calculated (mg g ⁻¹)	15.50 ± 0.06	18.6 ± 0.7
	k ₁ (min ⁻¹)	0.040 ± 0.002	0.12 ± 0.03
	R ²	0.99977	0.999695
	AIC	58.5773	13.72887
Pseudo-second-order (PSO)	q _e ¹ , calculated (mg g ⁻¹)	17.8 ± 0.1	22 ± 2
	k ₂ (g mg ⁻¹ min ⁻¹)	0 ± 6	0.006 ± 0.003
	R ²	0.99949	0.99703
	AIC	71.27913	13.50689
Elovich	a ² (mg g ⁻¹ min ⁻¹)	196 ± 258	10 ± 8
	b ³ (g mg ⁻¹)	0.65 ± 0.08	0.2 ± 0.0
	R ²	0.99899	0.99694

¹q_e = Adsorption capacity; ²a = Elovich model parameter; ³b = Elovich model parameter

Table S8. Parameters of the adsorption isotherm of Fe²⁺ and Mn²⁺ by HC6

Model	Parameter	Fe	Mn
Langmuir	q _m (mg g ⁻¹)	21 ± 3	34 ± 2
	K _L (L mg ⁻¹)	0.020 ± 0.007	0.010 ± 0.001
	R ²	0.995	0.9994
	AIC	21.47358	33.60851
Freundlich	K _F (mg g ⁻¹)/ (mg L ⁻¹) ^{1/n}	2.4 ± 0.8	15 ± 3
	n	2.6 ± 0.5	1.8 ± 0.1
	R ²	0.996	0.9991
	AIC	18.83262	36.35065

Table S9. Evaluation of interferences on the removal efficiency of Fe²⁺ and Mn²⁺ by HC6

	Redox potential	Conductivity	q _{eFe}	q _{eMn}
	(mV)	(μS/cm)	(mg g ⁻¹)	(mg g ⁻¹)
Type II water	446	0.95	15.50 ± 0.06	22 ± 2
Tap water	408	189	13 ± 2	18.0 ± 0.1