Supporting Information

Ionothermal Carbonization in [Bmim][$FeCl_4$]: an Opportunity for the Valorization of Raw Lignocellulosic Agrowastes into Advanced Porous Carbons for CO_2 Capture†

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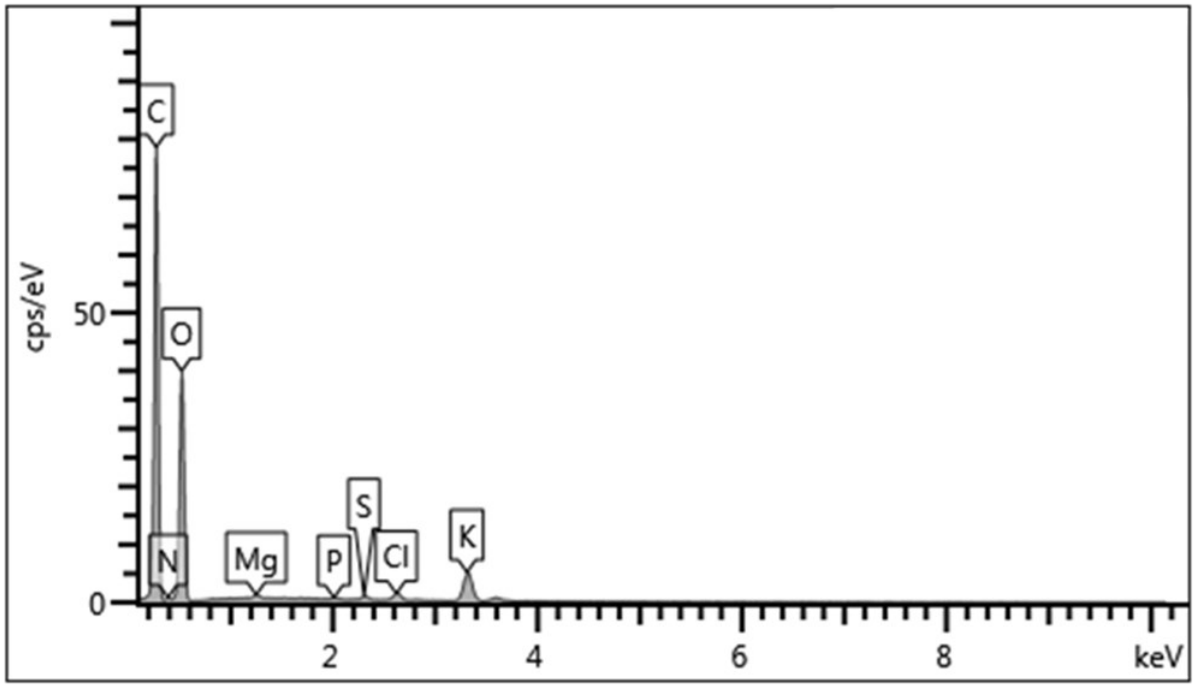


Figure S1. EDX spectrum of raw cocoa shell (CS).

Table S1. SEM-EDX analysis of raw cocoa shell (CS).

Chemical element	wt.%	at.%
C	55.36	63.61
N	1.52	1.49
O	38.44	33.16
Mg	0.21	0.12
P	0.09	0.04
S	0.22	0.10
Cl	0.60	0.23
K	3.56	1.25
Total:	100.00	100.00

Table S2. Elemental and chemical composition of cocoa shell (CS).

	wt.%	TGA under air wt%		Elemental Analysis (EA) wt.%				SEM-EDX wt%	
	Lignin Klason	Water	Ash	C	H	O	N	K	Others
CS	28.7	7.5	5.8	43.3†	5.9†	46.5†	0.7†	3.7†	1.1†

†The total amount exceeds 100 wt% because SEM-EDX is not quantitative and overestimates some elements.

Table S3. Mass yield, carbon yield and elemental composition of hydrochars and ionochars obtained at 240°C.

	wt.%			Elemental Analysis (EA) wt.%				SEM-EDX wt%	
	Mass Yield	Corrected Mass Yield	Carbon Yield	C	H	O	N	Fe	Cl
CS	n/a	n/a	n/a	43.3	5.9	46.5	0.7	0	0
HC-240	27	27	45	70.9	5.3	22.3	1.6	0	0
HC-Fe-240	28	27.7	46	71.8	3.1	23.7	0.2	0	1.2
IC-240	25	23.8	39.5	71.6	n/a	n/a	6.7	0	0
IC-Fe-240	47	43.4	73	67.1	3.8	26.8	1.4	3.5	4.3

†The total amount exceeds 100 wt% because SEM-EDX is not quantitative and overestimates some elements.

Table S4. Textural properties obtained from nitrogen sorption isotherms at 77 K of hydrochars and ionochars obtained at 240°C.

	Specific Surface Area ($m^2\ g^{-1}$)			Volume ($cm^3\ g^{-1}$)		
	SSA_{BET}	$SSA_{micropore}$	$SSA_{external}$	V_{total}	$V_{micropore}$	$V_{external}$
HC-240	20	0	20	0.19	0	0.19
HC-Fe-240	284	156	128	0.6	0.06	0.54
IC-240	< 1	n/a	n/a	n/a	n/a	n/a
IC-Fe-240	550	438	112	0.46	0.2	0.26

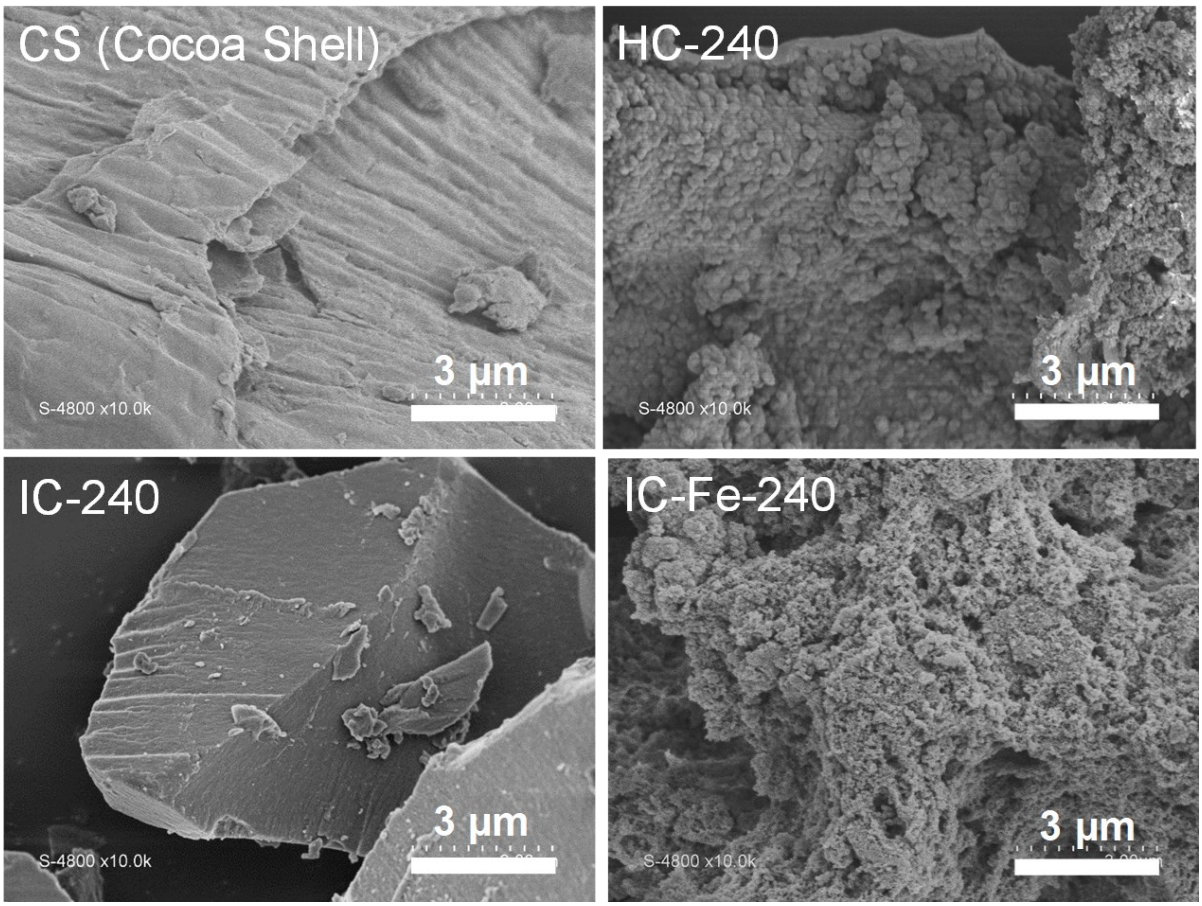
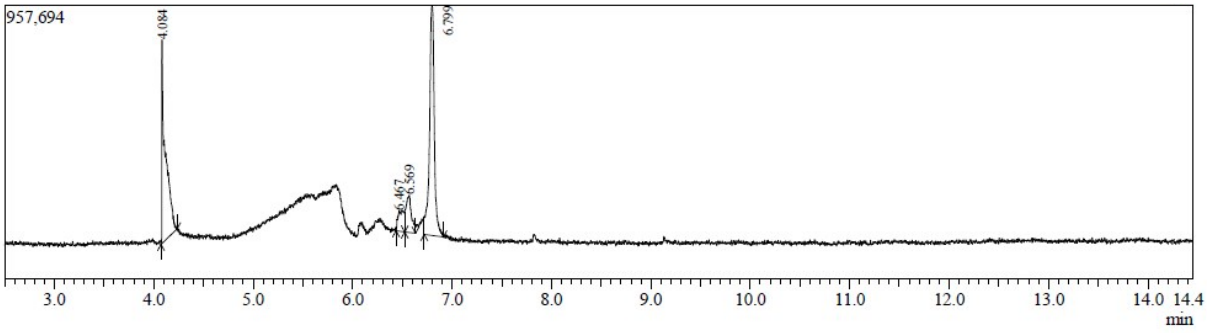


Figure S2. Scanning electron microscopy of raw cocoa shell (CS) and CS-derived hydrochar (**HC-240**) and ionochars (**IC-240** and **IC-Fe-240**) obtained at 240°C.



Peak Report

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Name
1	4.084	4.073	4.233	1734196	33.28	711100	1H-Imidazole, 1-methyl-
2	6.467	6.437	6.523	304734	5.85	71943	1-Butylimidazole
3	6.569	6.523	6.633	499690	9.59	129795	N-Propionylimidazole
4	6.799	6.720	6.913	2672381	51.28	803582	1-Butylimidazole
				5211001	100.00	1716420	

Figure S3. GC-MS of [Bmim]Cl recovered after ITC of CS at 240°C for 20 h.

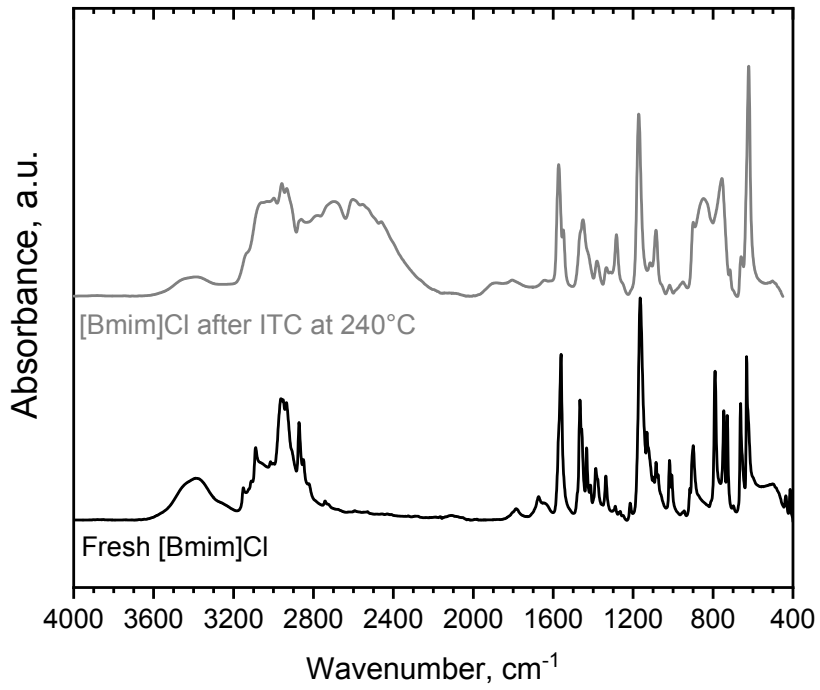


Figure S4. FTIR spectra of fresh [Bmim]Cl and [Bmim]Cl recovered after ITC of CS at 240°C for 20 h.

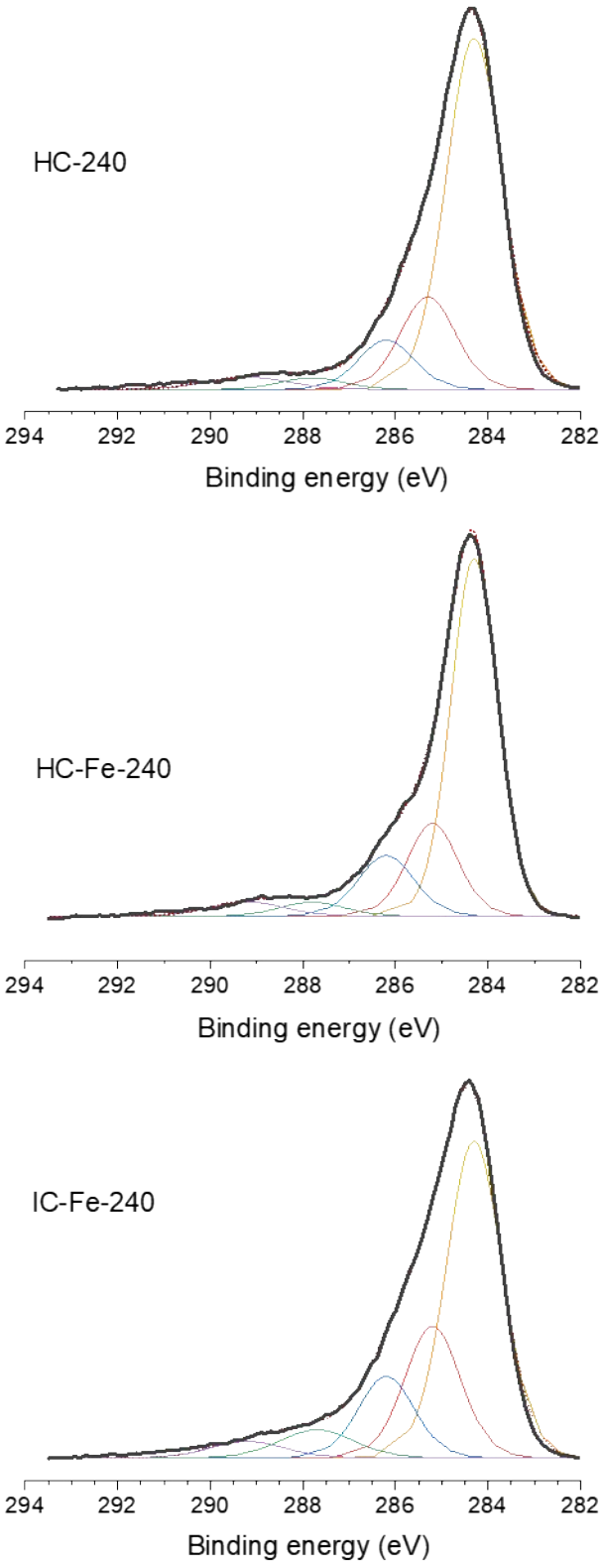


Figure S5. C1s X-ray photoelectron spectroscopy band-like spectra (black solid lines) and deconvoluted curves (colored solid lines) of **HC-240**, **HC-Fe-240** and **IC-Fe-240**.

Table S5. XPS data obtained from the deconvoluted C1s spectra of hydrochars and ionochars obtained at 240°C.

	XPS at.%					
Position (eV)	284.3	285.2	286.2	287.7	289.2	711
Function	Csp2	Csp3	C-O	C=O	COOR	Fe
IC-Fe-240	53.7	22.3	13.9	6.4	3.8	0.7
HC-240	67	17.5	9.4	2.6	3.5	n/a
HC-Fe-240	62.2	17.7	12.7	3.4	4.0	n/a

Table S6. XPS data obtained from the deconvoluted O1s spectra of hydrochars and ionochars obtained at 240°C.

	XPS at.%			O/C mass ratio	
				XPS	EA
Position (eV)	531.4	533.0	534.5	n/a	n/a
Function	C-O-C and/or Fe-O-C	C=O	Strong electronegativity	n/a	n/a
IC-Fe-240	35	58	7	0.27	0.40
HC-240	29	71	0	0.26	0.31
HC-Fe-240	29	69	2	0.28	0.33

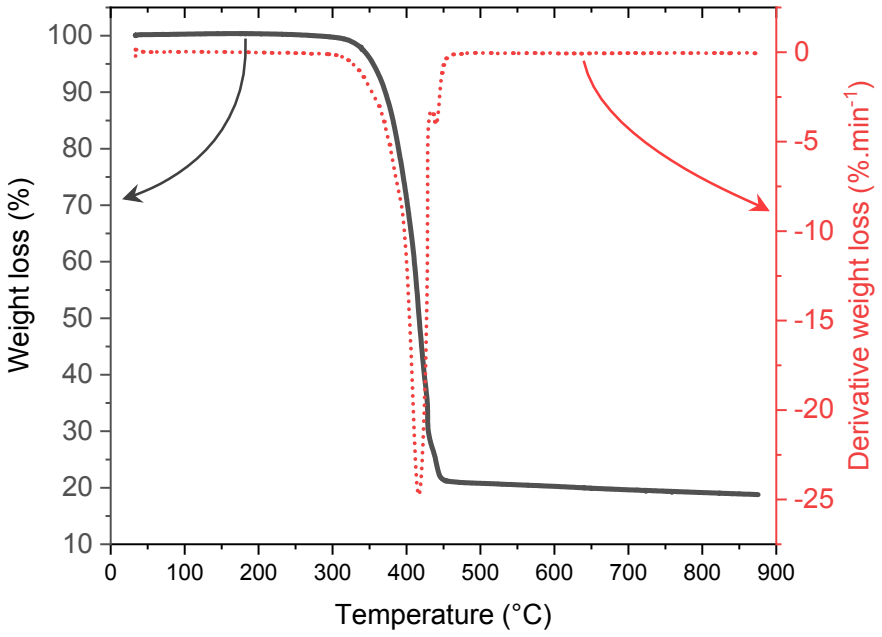


Figure S6. TGA of [Bmim][$FeCl_4$] under air at 10 °C min^{-1}.

Table S7. **Water content**. Mass yield, carbon yield and elemental composition of hydrochars and ionochars obtained at 240°C.

	wt.%			Elemental Analysis (EA) wt.%			SEM-EDX wt%	
	Mass Yield	Corrected Mass Yield	Carbon Yield	C	H	N	Fe	Cl
HC-240	27	27	45	70.9	5.3	1.6	0	0
IC-Fe-240-25w	41	38.4	61.6	69	3.9	0.6	5.4	1
IC-Fe-240-10w	43	40.4	68.8	68.8	3.4	1	2.9	3.2
IC-Fe-240-2w	47	43.5	74.8	67.7	3.4	1.3	2.8	4.6
IC-Fe-240	47	43.4	73	67.1	3.8	1.4	3.5	4.3

Table S8. **Water content**. Textural properties obtained from nitrogen sorption isotherms at 77 K of ionochars obtained at 240°C.

	Specific Surface Area ($m^2\ g^{-1}$)			Volume ($cm^3\ g^{-1}$)		
	SSA_{BET}	$SSA_{micropore}$	$SSA_{external}$	V_{total}	$V_{micropore}$	$V_{external}$
HC-240	20	0	20	0.19	0	0.19
IC-Fe-240-25w	474	395	79	0.37	0.17	0.2
IC-Fe-240-10w	616	476	140	0.57	0.21	0.36
IC-Fe-240-2w	566	434	132	0.52	0.19	0.33
IC-Fe-240	550	438	112	0.46	0.2	0.26

Table S9. Biomass composition. Mass yield, carbon yield and elemental composition of ionochars obtained at 240°C from cellulose (C), cocoa shell, klason lignin (KL) and commercial kraft lignin (L).

	wt.%			Elemental Analysis (EA) wt.%			SEM-EDX wt%	
	Mass Yield	Corrected Mass Yield	Carbon Yield	C	H	N	Fe	Cl
IC-Fe-240-C	47	44	79.3	70.7	3.5	0.3	2.3	4.1
IC-Fe-240	47	43.4	73	67.1	3.8	1.4	3.5	4.3
IC-Fe-240-KL	83	75.5	91.3	65.1	3.8	1.7	2.8	6.2
IC-Fe-240-L	96	85.6	92.3	59.7	2.4	0.7	6.1	4.7

Table S10. **Biomass composition**. Textural properties obtained from nitrogen sorption isotherms at 77 K of ionochars obtained at 240°C from cellulose (C), cocoa shell, klason lignin (KL) and commercial kraft lignin (L).

	Specific Surface Area ($m^2\ g^{-1}$)			Volume ($cm^3\ g^{-1}$)		
	SSA_{BET}	$SSA_{micropore}$	$SSA_{external}$	V_{total}	$V_{micropore}$	$V_{external}$
IC-Fe-240-C	736	688	48	0.61	0.34	0.27
IC-Fe-240	550	438	112	0.46	0.2	0.26
IC-Fe-240-KL	250	216	34	0.17	0.09	0.08
IC-Fe-240-L	42	14	28	0.15	0	0.15

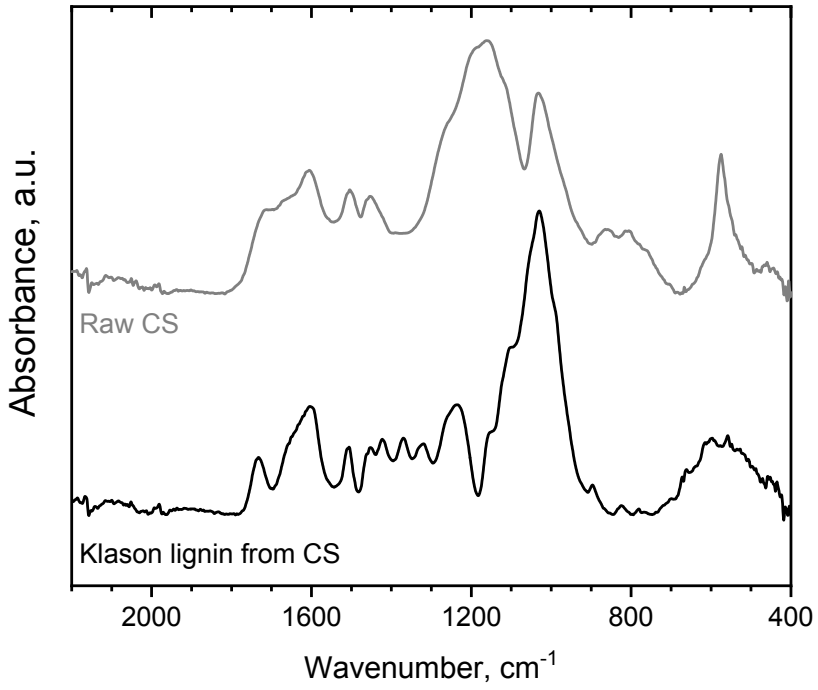


Figure S7. FTIR spectra of raw CS and Klason lignin.

Table S11. **Recycling**. Mass yield, carbon yield and elemental composition of ionochars obtained at 240°C from fresh $BmimFeCl_4$ (**IC-Fe-240**) and from recycled $BmimFeCl_4$ (**IC-Fe-240-r1**).

	wt.%			Elemental Analysis (EA) wt.%			SEM-EDX wt%	
	Mass Yield	Corrected Mass Yield	Carbon Yield	C	H	N	Fe	Cl
IC-Fe-240	47	43.4	73	67.1	3.8	1.4	3.5	4.3
IC-Fe-240-r1	45.4	42.4	72.6	68.7	3.3	1.5	3.4	3.3

Table S12. **Recycling**. Textural properties obtained from nitrogen sorption isotherms at 77 K of ionochars obtained at 240°C from fresh $BmimFeCl_4$ (**IC-Fe-240**) and from recycled $BmimFeCl_4$ (**IC-Fe-240-r1**).

	Specific Surface Area ($m^2\ g^{-1}$)			Volume ($cm^3\ g^{-1}$)		
	SSA_{BET}	$SSA_{micropore}$	$SSA_{external}$	V_{total}	$V_{micropore}$	$V_{external}$
IC-Fe-240	550	438	112	0.46	0.2	0.26
IC-Fe-240-r1	455	354	101	0.4	0.15	0.25

Table S13. **Pyrolysis**. Textural properties obtained from nitrogen sorption isotherms at 77 K of ionochars obtained at 240°C and pyrolyzed at 900°C under argon (**P9**).

	Specific Surface Area ($m^2\ g^{-1}$)			Volume ($cm^3\ g^{-1}$)		
	SSA_{BET}	$SSA_{micropore}$	$SSA_{external}$	V_{total}	$V_{micropore}$	$V_{external}$
IC-Fe-240	550	438	112	0.46	0.2	0.26
IC-Fe-240-P9	552	479	73	0.35	0.2	0.15
IC-Fe-240-10w-P9	640	497	143	0.62	0.2	0.42
HC-240-P9	249	215	34	0.25	0.09	0.16
HC-Fe-240-P9	530	407	123	0.61	0.16	0.45
CS-P9	< 1	n/a	n/a	n/a	n/a	n/a

Table S14. **Pyrolysis**. Mass yield, carbon yield and elemental composition of ionochars obtained at 240°C and pyrolyzed at 900°C under argon (**P9**).

	wt.%			Elemental Analysis (EA) wt.%			SEM-EDX wt%	
	Mass Yield	Corrected Mass Yield	Carbon Yield	C	H	N	Fe	Cl
IC-Fe-240	47	43.4	73	67.1	3.8	1.4	3.5	4.3
IC-Fe-240-P9	63	n/a	83.9	89.4	0.6	1.5	1.8	0
IC-Fe-240-10w-P9	66	n/a	78.1	81.4	1.6	0.8	1.9	0
HC-240-P9	56	n/a	69.9	88.5	0.6	1.6	n/a	n/a
HC-Fe-240-P9	63	n/a	81.2	92.5	0.2	0.2	0.5	0
CS-P9	30	n/a	48.4	69.8	1.3	0.9	n/a	n/a

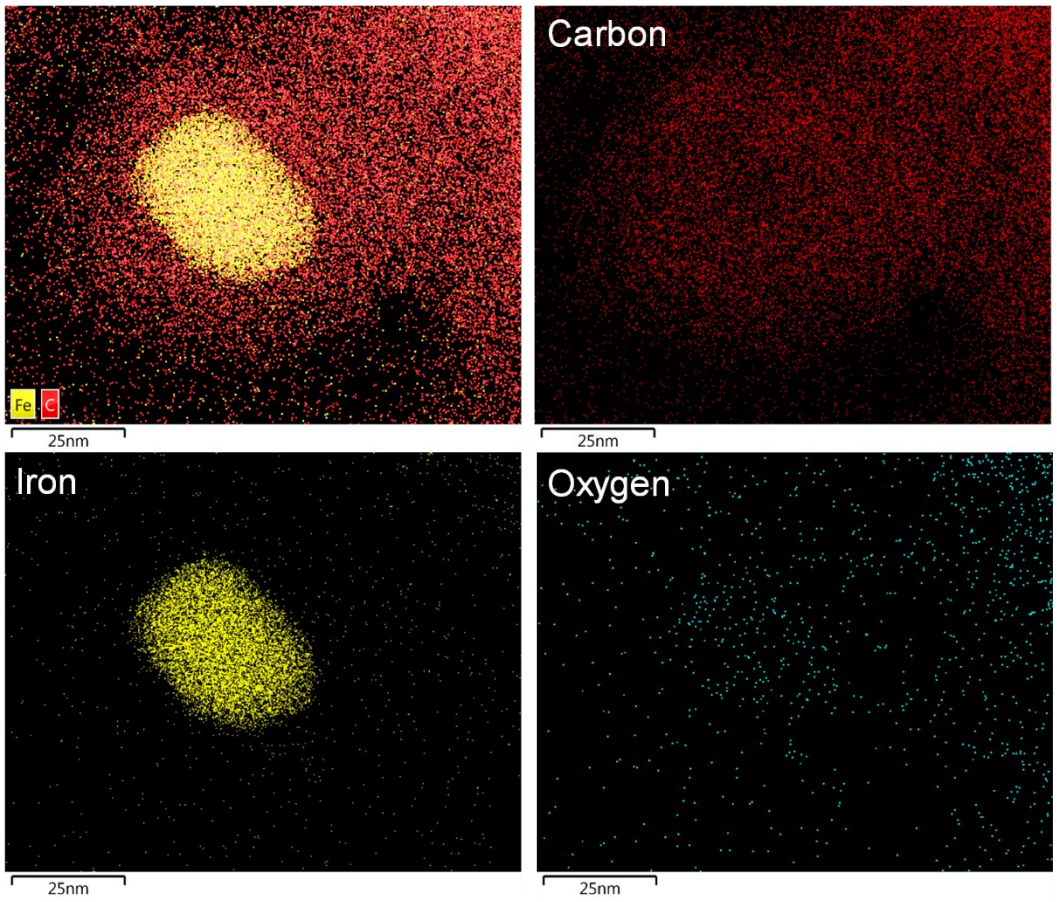


Figure S8. STEM EDX mapping of **IC-Fe-240-P9**.

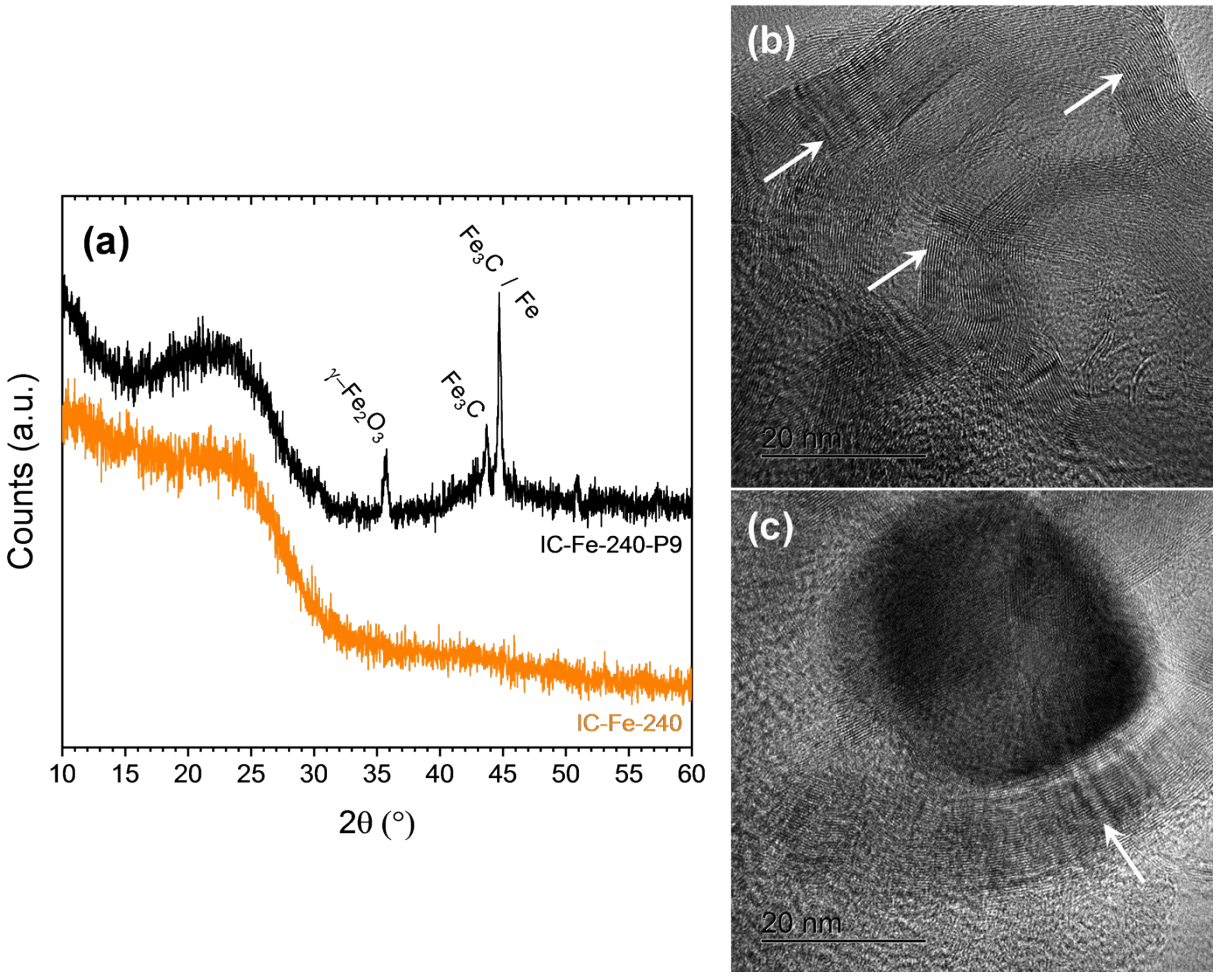


Figure S9. (a) XRD patterns of **IC-Fe-240** and **IC-Fe-240-P9**. (b-c) HR-TEM of **IC-Fe-240-P9**. The white arrows indicate the graphitic layers.

Table S15. **CO_2 activation**. Textural properties obtained from nitrogen sorption isotherms at 77 K of ionochars obtained at 240°C and pyrolyzed at 900°C under argon (**P9**) or activated at 950°C under CO_2 (**A1**, **A2**).

	Specific Surface Area ($m^2\ g^{-1}$)			Volume ($cm^3\ g^{-1}$)		
	SSA_{BET}	$SSA_{micropore}$	$SSA_{external}$	V_{total}	$V_{micropore}$	$V_{external}$
IC-Fe-240-10w	616	476	140	0.57	0.21	0.36
IC-Fe-240-10w-P9	640	497	143	0.62	0.2	0.42
IC-Fe-240-10w-A1	1441	1214	227	1.19	0.5	0.69
IC-Fe-240-10w-A2	2065	1778	287	1.59	0.73	0.86
HC-240-A1	807	784	23	0.47	0.31	0.16

Table S16. **CO_2 activation**. Mass yield, carbon yield and elemental composition of ionochars obtained at 240°C and pyrolyzed at 900°C under argon (**P9**) or activated at 950°C under CO_2 (**A1**, **A2**).

	wt.%			Elemental Analysis (EA) wt.%			SEM-EDX wt%	
	Mass Yield	Corrected Mass Yield	Carbon Yield	C	H	N	Fe	Cl
IC-Fe-240-10w	43	40.4	68.8	68.8	3.4	1	2.9	3.2
IC-Fe-240-10w-P9	66	n/a	78.1	81.4	1.6	0.8	1.9	0
IC-Fe-240-10w-A1	37	n/a	39.5	73.5	1.9	0.4	1.4	0
IC-Fe-240-10w-A2	35	n/a	35.5	69.8	2.1	0.4	3.3	0
HC-240-A1	44	n/a	44.8	72.2	2.2	1.6	n/a	n/a

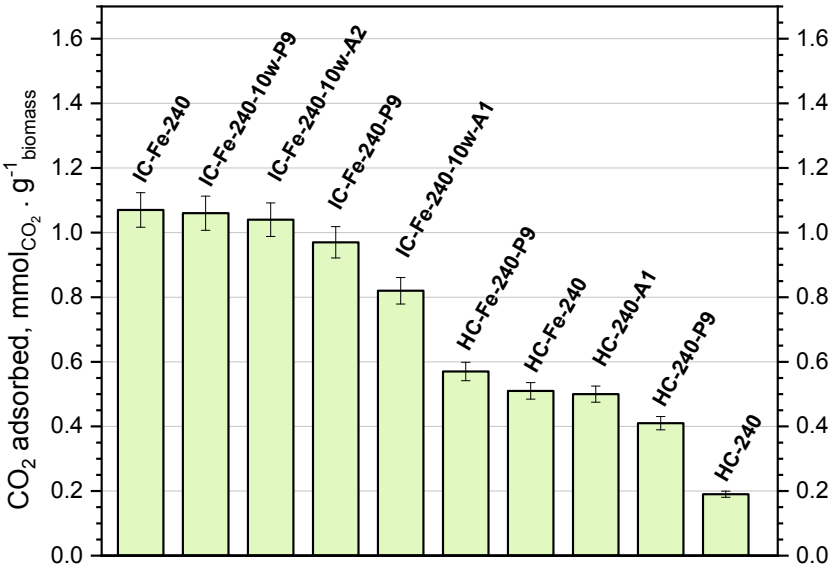


Figure S10. CO_2 uptake at 273 K of each sample expressed per gram of CS treated.