Design of Functionalized Biochars for Dual Wastewater Treatment and Fertilizer Production

Supplementary Material

Section S1

Adsorption experiments

With a view to, ammonium chloride (2.972 g; NH_4Cl) was dissolved in 1 L of ultrapure water to obtain a mother solution of ammonium ions with a concentration of 1000 mg/L ($[NH_4^+]$). The adsorption experiments were conducted using ultrapure water produced by Adrona Crystal equipment with an electrical conductivity of 0.055 μS/cm (ADRONA SIA, model EX-1101, Latvia).

Pilot experiments were performed to determine the best performance of ammonium ions adsorption capacity such as biochar dosage, pH of the solution, and the optimal contact time. Therefore, the ammonium concentration was set to 75 mg NH_4^+/L at pH 7 (neutral) in 200 mL of ultrapure water at environment temperature. Then, 200, 400, 600, 800, and 1000 mg of biochar were added and stirred to determine the ideal dose. Control concentrations were measured at the beginning of the experiments and then at 2 hours of contact time. As soon as the ideal dose of biochar was determined, the optimal pH of the solution was explored, keeping the other variables constant (adsorbent dose, contact time, solution temperature). The pH values studied were 3, 5, 7, and 9. Lastly, to analyse the adsorption of NH^+ as a function of contact time, we took numerous samples (initial concentration 75 mg/L NH_4^+, pH 9, and 800 mg biochar dose) every 10 minutes during the first hour and every 20 minutes until the second hour.

Batch experiments were conducted to obtain the isotherms by adding biochar samples to water solutions with different initial NH_4^+ concentration. Experiments were conducted at pH 9 and with 800 mg poplar chop-derived biochar dose, using 200 mL of solutions with an initial concentration of 10, 30, 50, 75, and 100 mg NH_4^+/L. The suspensions were stirred for 80 minutes at 250 rpm, followed by sampling (2 mL) and filtering through 0.45 μm microporous membrane filters. Ammonium ions concentration was measured using a Merck Spectroquant Nova 60 spectrophotometer.

Section S2

Once the adsorption experiments were finished, the solution was filtered using paper (size 205 mm, medium filtration rate, particle retention 5–13 μm; VWR International, Germany), subsequently, it was dried at room temperature and the collected material was stored to be used in germination and planting experiments.

Germination experiments

Nasturtium officinale seeds were used for investigating the effect of biochars recovered with ammonium ions on seed germination and early root development of

higher plants in the present research work. The surface that contained the seeds was sterilized with 96% v/v ethanol (Molar Chemicals KFT, HU) during one minute and washed with ultrapure water several times. A filter paper was arranged in plastic Petri dishes with diameter 8.5 cm (VWR); ten seeds were placed. The filter papers were moistened with 3mL of ultra-pure water in the case of control and the rest with solutions of different recovery biochars contained ammonium ions and the mix of phosphates ions and ammonium in three different concentrations 1.25 % m/v, 3.1% m/v and 5% m/v. The experiments were repeated three times. Each Petri dish was closed but not sealed, and then the seeds were left to germinate (25 °C in the dark). After 4 days, each seed with visible roots was counted as germinated, and the length of the primary root was measured. In total 840 seeds were used for germination experiments included the control.

Pot experiments and factorial design analysis

Design of experiments (DOE) is commonly used to systematically investigate the influence of experimental variables on process performance. In the present study, a central composite design (CCD) was applied to structure the pot experiments and to evaluate the influence of pyrolysis temperature and biochar dose on plant growth. Two factors were considered in the experimental design: pyrolysis temperature (300–500 °C) and biochar dose (1.25–5 % m/m). The design included factorial points and center points to explore the response of the system across the selected experimental range. The factors and levels used in the experimental design are presented in Table S1. In addition, three types of poplar-derived biochars (non-modified, alkaline-modified, and acid-modified) were tested. For each biochar type, the experimental runs were performed with four repetitions to ensure reproducibility of the planting experiments.

Table S1. Factors and levels used in the CCD for fertilize plants using recovery poplar chop-derived biochar and ammonium ions.

Factor	Code	Low level (-1)	Centre point (0)	High level (+1)
Pyrolysis temperature (°C)	A	300	400	500
Biochar dose % (m/m)	B	1.25	3.1	5

Planting experiments

The indoor planting experiments were carried out in order to examine the effect of using the different recovery biochars enriched with ammonium ions, Nasturtium officinale was one more time the selected plant for this study. The soil was mixed with the recovery biochars in three concentration 1.25% m/m, 3.1% m/m and 5% m/m. Then 40 g of the mixture were added in the seeding tray (ProGarden, 33x23x13 cm, China), five seeds were placed in each compartment, in total 740 seeds were planted included the control. The seeding trays were labelled and located in the shelfs under a led lamp (KERTLAP ZH-GLS25W001,60Hz, Hungary). The number of repetitions were guided by the factorial design. After 14 days, plant habits of rapeseed seedlings were recorded and harvested. Then, the basic morphological parameters were measured including the number of leaves, the stem size, in addition to fresh weight of biomass.

Section S3

SEM analysis of poplar chop biochars

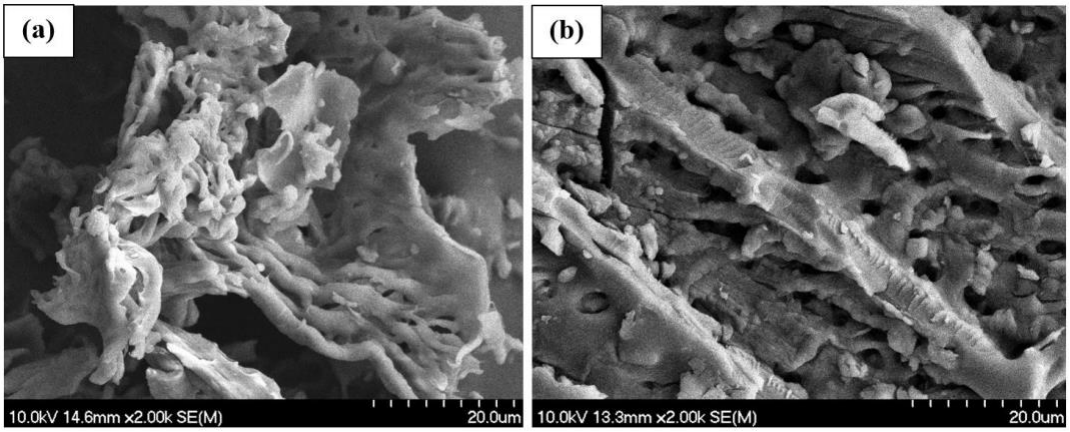


Figure S1. Scanning electron microscope images of PCB_300: (a) beforeNH_4^+ adsorption onto biochar surface and (b) after NH_4^+ adsorption onto biochar surface

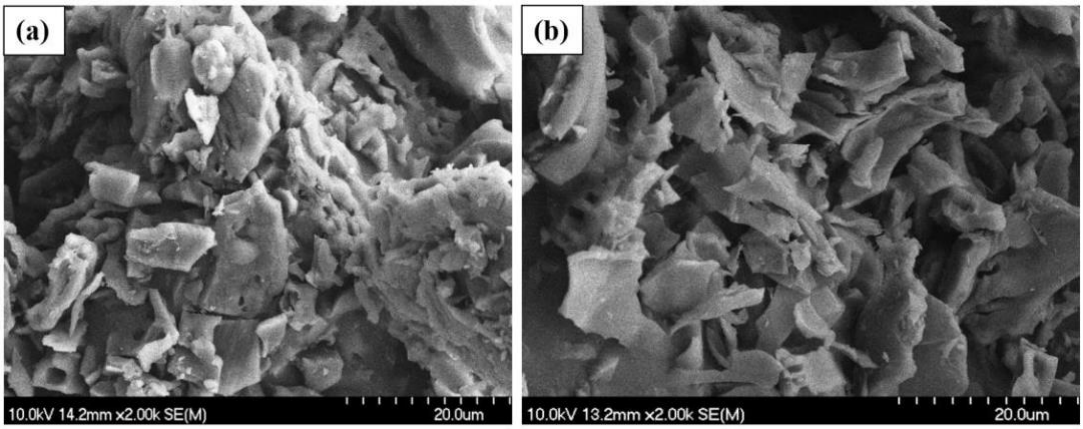


Figure S2. Scanning electron microscope images of PCB_400: (a) before NH_4^+ adsorption onto biochar surface and (b) after NH_4^+ adsorption onto biochar surface

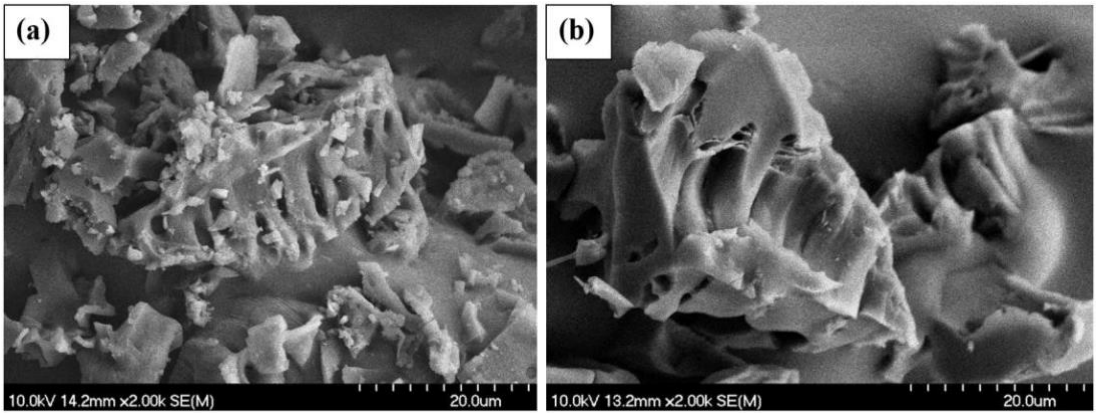


Figure S3. Scanning electron microscope images of PCB_500: (a) before NH_4^+ adsorption onto biochar surface and (b) after NH_4^+ adsorption onto biochar surface a) before NH_4^+ removal and b) after NH_4^+ removal.

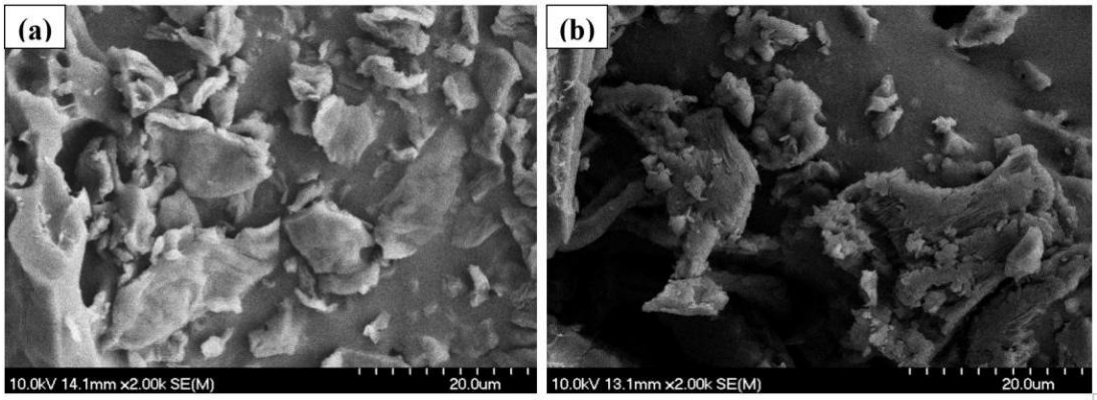


Figure S4. Scanning electron microscope images of PCalB_300: (a) before NH_4^+ removal and (b) after NH_4^+ removal.

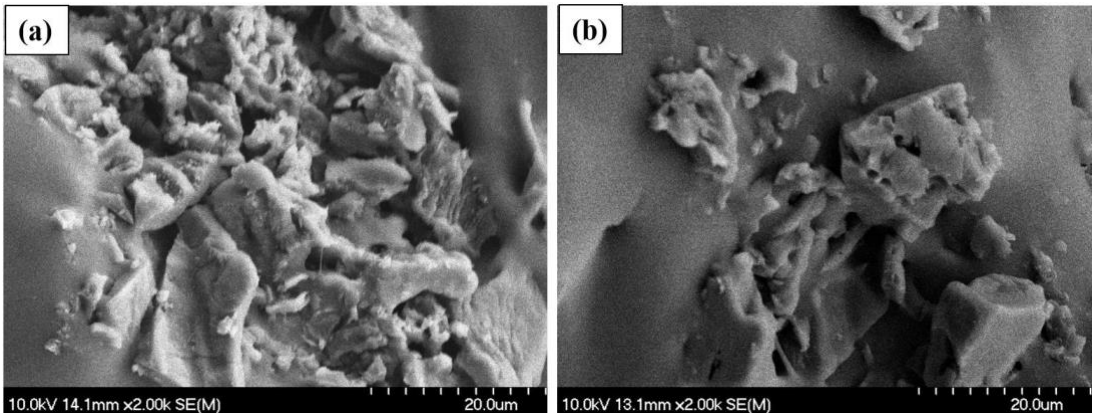


Figure S5. Scanning electron microscope images of PCalB_400: (a) before NH_4^+ adsorption onto biochar surface and (b) after NH_4^+ adsorption onto biochar surface

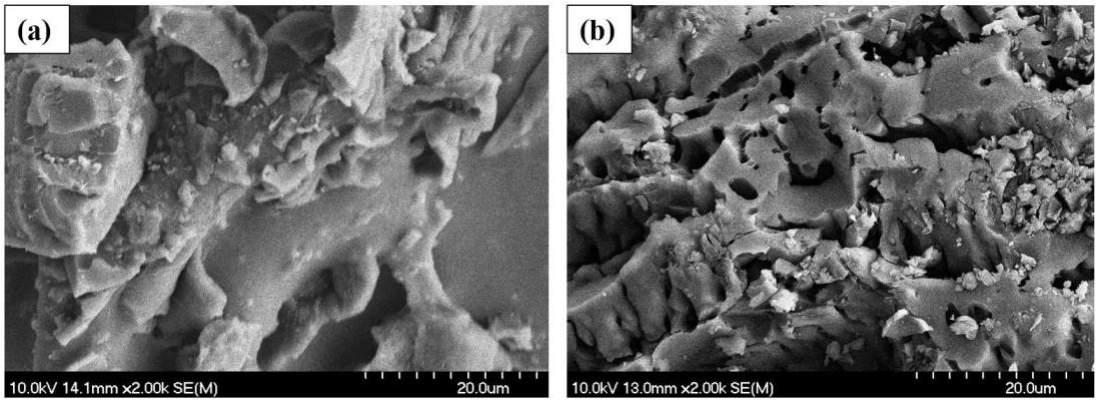


Figure S6. Scanning electron microscope images of PCalB_500: (a) before NH_4^+ adsorption onto biochar surface and (b) after NH_4^+ adsorption onto biochar surface a) before NH_4^+ removal and b) after NH_4^+ removal.

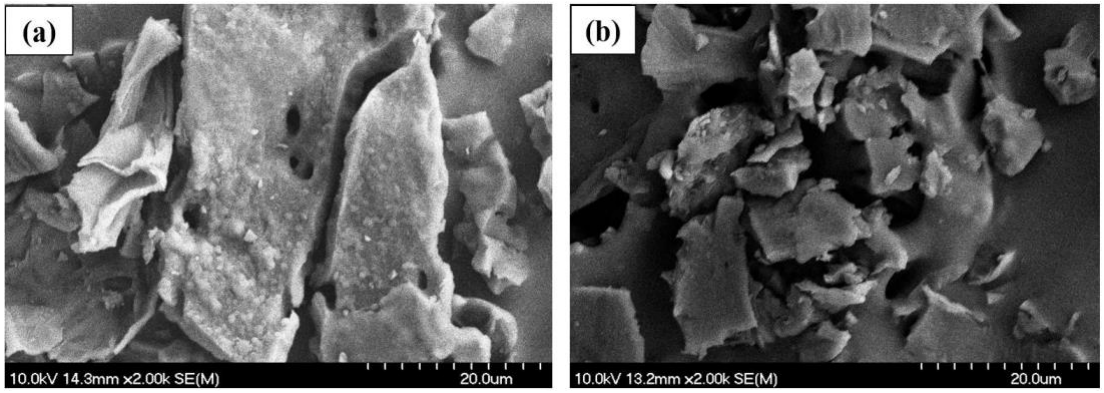


Figure S7. Scanning electron microscope images of PCacB_300: a) before NH_4^+ removal and b) after NH_4^+ removal.

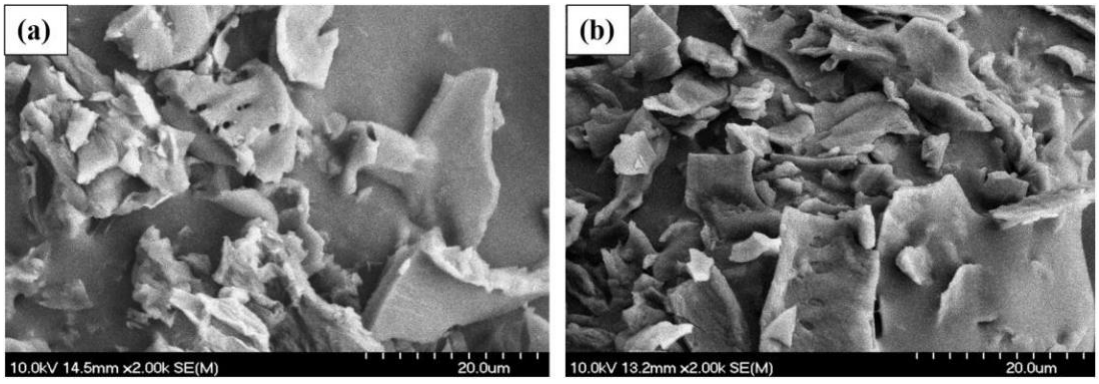


Figure S8. Scanning electron microscope images of PCacB_400: (a) before NH_4^+ adsorption onto biochar surface and (b) after NH_4^+ adsorption onto biochar surface

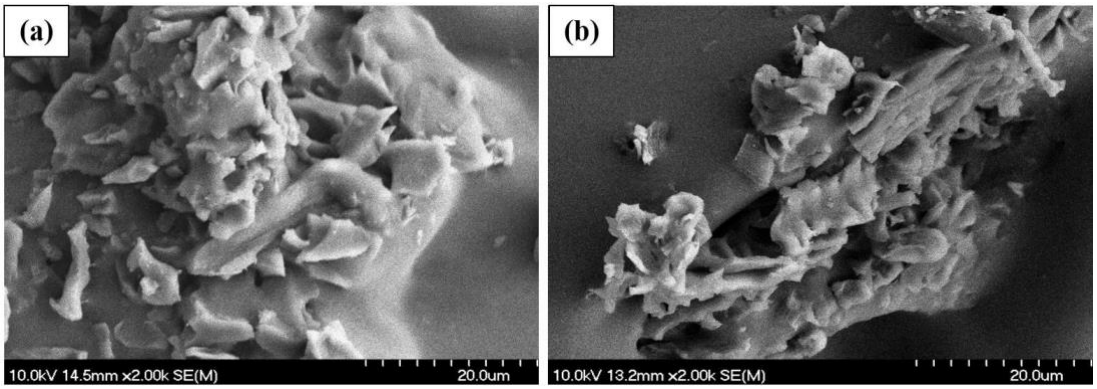


Figure S9. Scanning electron microscope images of PCacB_500: (a) before NH_4^+ adsorption onto biochar surface and (b) after NH_4^+ adsorption onto biochar surface

EDX analysis of biochars pyrolized at 300°C, 400°C and 500°C

Table S2. Elemental composition of non-modified poplar chop-derived biochar materials obtained at various pyrolysis temperatures.

Elemental content (%)	Non modified poplar chop-derived biochars					
	300 °C ba*	300 °C aa**	400 °C ba	400 °C aa	500 °C ba	500 °C aa
C	49.19±6.36	47.14±6.13	55.41±8.15	58.93±9.54	59.79±9.54	62.83±11.0
O	50.27±8.92	52.48±10.16	44.21±7.01	40.61±6.30	39.14±5.56	37.02±5.41
Si	0	0.065±0.0	0	0.15±0.0	0	0.038±0.0
P	0	0.086±0.0	0	0.037±0.0	0	0
K	0.44±0.0	0.23±0.0	0.37±0.0	0.28±0.0	1.05±0.0	0.12±0.0
Ca	0.10±0.0	0	0.016±0.0	0	0.026±0.0	0

Table S3. Elemental composition of alkaline-modified poplar chop-derived biochar materials obtained at various pyrolysis temperatures.

Elemental content (%)	Alkaline poplar chop-derived biochars					
	300 °C ba*	300 °C aa**	400 °C ba	400 °C aa	500 °C ba	500 °C aa
C	46.54±5.86	52.60±7.73	63.75±11.27	53.02±7.85	62.53±10.75	60.28±10.07
O	50.11±8.86	42.02±8.38	34.66±4.58	46.43±8.40	35.38±4.67	39.35±5.96
Na	2.29±0.008	0.28±0.0	1.20±0.0	0.48±0.0	1.66±0.006	0.33±0.0
Mg	0.49±0.0	0	0.18±0.0	0	0.21±0.0	0
Si	0.064±0.0	0	0.06±0.0	0	0.067±0.0	0
P	0	0	0	0	0	0
K	0.054±0.0	0.095±0.0	0.059±0.0	0.074±0.0	0.070±0.0	0.043±0.0
Ca	0.45±0.0	0	0.089±0.0	0	0.080±0.0	0

Table S4. Elemental composition of acid-modified poplar chop-derived biochar materials obtained at various pyrolysis temperatures.

Elemental content (%)	Acidic poplar chop-derived biochars					
	300 °C ba*	300 °C aa**	400 °C ba	400 °C aa	500 °C ba	500 °C aa
C	60.45±9.85	61.84±10.93	65.1±11.56	50.98±7.15	64.83±11.45	53.90±8.10
O	39.46±5.64	37.81±5.75	34.75±4.47	48.76±8.82	34.99±4.50	45.78±7.97
Na	0	0.31±0.0	0	0.18±0.0	0	0.2±0.0
Si	0.016±0.0	0	0.026±0.0	0	0.061±0.0	0
Cl	0.004±0.0	0	0	0	0	0
K	0.059±0.0	0.04±0	0.08±0.0	0.075±0.0	0.087±0.0	0.10±0.0
Ca	0.013±0.0	0	0.034±0.0	0	0.028±0.0	0

FT-IR measurements

Table S5. Functional groups identified in the non-modified poplar chop-derived biochars.

Wavenumber (cm^{-1})				
PCB_300	**PCB_400**	**PCB_500**	**Functional groups**	**References**
804	811	923	N–H, C–H	(Nandiyanto et al., 2019)
1093	955	-	C–N, C–O, Si–O–Si	
1213	1219	-	C=O, O–H, C–O–C	
1450	1443	1488	N–H, C–C	
1543	1516	-	N–H, C=C, C=O	
1610	1597	1583	N–H, C=C, C=O	
1668	-	-	N–H, C=C, C=O	
1701	1691	1692	C=O	
1834	1784	-	C=O	
-	2324	-	C=O	
2386	2370	2363	C=O	
2928	2930	-	C–H, $–CH_3$ or $–CH_2$	
3422	3416	-	O–H and N–H	
3684	3695	3672	O–H	

Table S6. Functional groups identified in the alkali-modified poplar chop-derived biochars.

Wavenumber (cm^{-1})				
PCalB_300	**PCalB_400**	**PCalB_500**	**Functional groups**	**References**
770	-	727	N–H, C–H	(Nandiyanto et al., 2019)
874	883	880	N–H, C–H	
1072	-	922	C–N, C–O, Si–O–Si	
1234	-	-	C=O, O–H, C–O–C	
1443	1323	1447	N–H, C–C	
1485	1450	1529	N–H, C=C, C=O	
1599	1502	1584	N–H, C=C, C=O	
1661	1690	-	N–H, C=C, C=O	
1701	1746	1763	C=O	
1805	-	-	C=O	
2345	-	-	C=O	
2367	2367	2364	C=O	
2926	2997	-	C–H, $–CH_3$ or $–CH_2$	
3425	-	-	O–H and N–H	
3694	3688	3703	O–H	

Table S7. Functional groups identified in the acidic-modified poplar chop-derived biochars.

Wavenumber (cm^{-1})				
PCacB_300	**PCacB_400**	**PCacB_500**	**Functional groups**	**References**
723	-	-	N–H, C–H	(Nandiyanto et al., 2019)
924	926	881	N–H, C–H	
1059	-	947	C–N, C–O, Si–O–Si	
1225	1244	1207	C=O, O–H, C–O–C	
1408	-	-	C–H, –COO	
1468	-	-	N–H, C=C, C=O	
1541	1505	-	N–H, C=C, C=O	
1603	1596	1593	N–H, C=C, C=O	
1672	1682	-	N–H, C=C, C=O	
1709	1798	1701	C=O	
1827	-	1809	C=O	
-	2361	2363	C=O	
2949	-	-	C–H, $–CH_3$ or $–CH_2$	
3369	-	3412	O–H and N–H	
3688	3685	3680	O–H	

Section S4

Kinetic and adsorption results

Table S8. Kinetic parameters for NH_4^+ adsorption using non-modified poplar chop-derived biochars

Kinetic Model	Parameters	PCB_300	PCB_400	PCB_500
Pseudo-first order (PFO)	q_e (mg/g)	3.98	3.70	2.30
	k_1	0.12	0.11	0.09
	R^2	0.84	0.55	0.93
	χ^2	0.18	0.29	0.44
Pseudo-second order (PSO)	q_e (mg/g)	4.34	4.01	2.56
	k_2	0.045	0.046	0.05
	R^2	0.91	0.70	0.95
	χ^2	0.095	0.18	0.32

Table S9. Kinetic parameters for NH_4^+ adsorption using alkaline-modified poplar chop-derived biochars

Kinetic Model	Parameters	PCalBC_300	PCalB_400	PCalB_500
Pseudo-first order	q_e (mg/g)	4.1	3.42	3.05
	k_1	0.15	0.04	0.04
	R^2	0.94	0.95	0.80
	χ^2	0.06	0.14	0.67
Pseudo-second order	q_e (mg/g)	4.32	4.13	3.52
	k_2	0.07	0.01	0.02
	R^2	0.93	0.97	0.87
	χ^2	0.07	0.08	0.45

Table S10. Kinetic parameters for NH_4^+ adsorption using acidic-modified poplar chop-derived biochars

Kinetic Model	Parameters	PCacBC_300	PCacB_400	PCacB_500
Pseudo-first order	q_e (mg/g)	2.46	3.38	2.46
	k_1	0.18	0.03	0.09
	R^2	0.97	0.82	0.90
	χ^2	0.08	0.66	0.41
Pseudo-second order	q_e (mg/g)	2.54	4.12	2.70
	k_2	0.20	0.01	0.05
	R^2	0.97	0.84	0.93
	χ^2	0.1	0.59	0.32

Table S11. Parameters of isotherms models for NH_4^+ adsorption using non modified poplar chop-derived biochars.

Biochar	Isotherm Model	Parameters	R^2	χ^2
PCB_300	Langmuir	K=0.0058 q_{max}=15.94 R_L=0.896	0.933	0.035
	Freundlich	K_f=0.131 1/n=0.842	0.917	0.051
	Temkin	b= 1024.22 A=0.093	0.995	0.015
PCB_400	Langmuir	K=0.048 q_{max}=12.96 R_L=0.912	0.950	0.019
	Freundlich	K_f=0.107 1/n=0.804	0.948	0.020
	Temkin	b=1371.57 A=0.086	0.990	0.028
PCB_500	Langmuir	K=0.069 q_{max}=2.611 R_L=0.421	0.998	0.001
	Freundlich	K_f=0.622 1/n=0.295	0.990	0.004
	Temkin	b=4577.90 A=0.80	0.999	0.003

Table S12. Parameters of isotherms models for NH_4^+ adsorption using alkali-modified poplar chop-derived biochars.

Biochar	Isotherm Model	Parameters	R^2	χ^2
PCalB_300	Langmuir	K=0.0033 q_{max}=28.27 R_L=0.94	0.987	0.006
	Freundlich	K_f=0.118 1/n=0.898	0.986	0.007
	Temkin	b= 1098.45 A=0.114	0.995	0.016
PCalB_400	Langmuir	K=0.0015 q_{max}=46.92 R_L=0.971	0.946	0.025
	Freundlich	K_f=0.088 1/n=0.926	0.947	0.028
	Temkin	b=1199.17 A=0.103	0.986	0.044
PCalB_500	Langmuir	K=0.0018 q_{max}=21.36 R_L=0.965	0.981	0.02
	Freundlich	K_f=0.018 1/n=1.16	0.991	0.011
	Temkin	b=1510.45 A=0.063	0.990	0.021

Table S13. Parameters of isotherms models for NH_4^+ adsorption using acidic-modified poplar chop-derived biochars.

Biochar	Isotherm Model	Parameters	R^2	χ^2
PCacB_300	Langmuir	K=0.0068 q_{max}=10.31 R_L=0.881	0.976	0.010
	Freundlich	K_f=0.115 1/n=0.793	0.968	0.015
	Temkin	b= 1445.11 A=0.0964	0.999	0.003
PCacB_400	Langmuir	K=0.0071 q_{max}=8.784 R_L=0.875	0.984	0.013
	Freundlich	K_f=0.058 1/n=0.925	0.991	0.008
	Temkin	b=1725.44 A=0.098	0.995	0.011
PCacB_500	Langmuir	K=0.0046 q_{max}=11.02 R_L=0.916	0.968	0.027
	Freundlich	K_f=0.071 1/n=0.856	0.964	0.035
	Temkin	b=1823.15 A=0.097	0.983	0.036