

Supporting Information

Fate of Copper in Saline-alkali Soil with Long-term (five consecutive crop seasons) Application of Biogas Residue

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Table S9 Total organic carbon content in saline-alkali soil, organic-free SAS and biogas residue.

S1 Additional descriptions about the experiments

X ray diffraction spectrum (XRD)

Saline-alkali soil and organic-free saline-alkali soil were made into directional plates according to the X ray diffraction requirements and determined by Bruker D2 PHASER. The determination conditions were CuK_α target radiation, a scanning speed 2°/min and a scanning range of 3–60°. The test and analysis were completed at the Jiangsu Academy of Agricultural

Sciences.

Fourier transform infrared spectrometry (FTIR)

KBr and incubated at 60 °C for 24 h. Then the samples were ground to 2 µm, mixed samples with KBr (1:100), and the lamination was made by a tableting machine before determination. Immediately thereafter, scanning was performed in the range of 400–4000 cm⁻¹, the number of scans were set to 16, and a resolution of 4 cm⁻¹ was used to record the spectra using Nicolet iS5 infrared spectrometers. The test was completed in the College of Science of Nanjing Agricultural University.

Isothermal titration calorimetry (ITC)

Isothermal heat drop quantitative experimental data were measured using a MicroCal iTC200 isothermal titration micro-calorimetric instrument at 60 °C that was stable 50 min, and the experimental temperature was set at 25 °C. Then, 200 µL of pH 5 absorbent was added to the ampoule and stirred with a gold rotor. When the heat flow was stable, 40 mM Cu²⁺ solution (pH 5) was dropped into the ampere flask with a syringe. The dilution heat was determined by the titration of 1 mM KNO₃ (pH 5) with Cu²⁺ solution. In order to calculate the thermodynamic parameters when the pure carboxyl, amino, sulpho and phosphate groups combined with Cu, the adsorption heat effects of Cu on four simple ligands (oxalic acid, glycine, sodium phosphate and sulfosalicylic acid, 1 mM) were measured. The titration steps were the same as above. Origin software was used for the processing of experimental data. The test was completed in the Centre of life Science Laboratory of Nanjing Agricultural University.

X-ray photoemission spectroscopy (XPS)

The chemical structures of samples were measured using Scanning XPS Microprobe PHI Quantera. The test conditions were that the target radiation was AlK_{α} and the analysis room air pressure was 6.7×10^{-8} Pa. Conductive adhesive was laid on the sample table and the sample was uploaded. The analysis area was $2.0 \times 2.0 \mu\text{m}$ (length \times width), the full spectrum scanning energy was 280 eV, the fine spectrum scanning energy was 69 eV, and the element binding energy by C 1s correction (284.8 eV). The test was completed at the Analysis and Testing Centre of the Nanjing University of Science and Technology.

Microzone X-ray fluorescence spectrum (Micro-XRF)

The samples were characterised by a Microzone X-ray fluorescence spectrometer (M4 tornado, Bruker, Germany). The test conditions were voltage of 50 kV, current of 600 μA , sample chamber pressure 20 mbar, and the Rh target was adopted. The test area was $22.2 \times 19.1 \text{ mm}$ (length \times width), the spot diameter was 15 μm and the spot step was 50 μm . The data were scanned twice, and the integration time of each point was 50 ms. The sample table movement rate was 1000 $\mu\text{m/s}$, and the test time of each sample was 2.45 h. The test was completed at Boyue Instruments (Shanghai) Co., Ltd.

Scanning electron microscope and energy dispersive spectrum (SEM-EDS)

The samples were characterised by a scanning electron microscope and energy dispersive spectrometer (HITACHI, S-3000N). The test was completed in the Life Science Laboratory Centre of Nanjing Agricultural University.

Table S1 The variety and relative amount of saline-alkali soils (Sal.S.) and organic-free saline-alkali soil (Sal.S.-O.C.).

	Sal.S.	Sal.S.-O.C.	Å		
Quartz	30.94%	24.77%	4.91		5.40
Berlinite	-	18.94%	4.90		10.84
Illite	3.87%	3.70%	5.24	9.03	10.14
Struvite-K	-	3.18%	6.89	6.17	11.14
Struvite	1.72%	-	6.96	6.14	11.22
Pyroxene	1.60%	2.20%	9.25	8.77	5.38
Calcite	0.60%	-	4.97		16.96
Sodalite	0.59%	-	9.04		
Hornblende	0.28%	-	9.83	18.06	5.30

“-” represents undetected

Table S2 Fitting parameters for adsorption isotherms of Cu on saline-alkali soil, organic-free saline-alkali soil and biogas residue.

Langmuir adsorption model			
$\frac{1}{Q_e} = \frac{1}{bQ} \cdot \frac{1}{C_e} + \frac{1}{Q}$			
	Q	$b(\times 10^{-5})$	R^2
Biogas residue	57.28 ± 7.14	25.69 ± 10.58	0.9975
Saline-alkali soil	23.21 ± 2.37	9.64 ± 7.74	0.9949
Organic-free saline-alkali soil	0.55 ± 0.017	97.82 ± 93.2	0.9923

Data represent the Mean \pm SE.

Table S3 Thermodynamic parameters for Cu adsorption in oxalic acid and glycine at pH 5 and 25°C in 1 mol/L KNO₃ electrolyte.

Titration	K (L/mol)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol)
Cu ²⁺ → carboxyl	1.57×10 ⁴	-12.0	-3.62	28.1
Cu ²⁺ → amino	1.80×10 ³	6.65	216	855

Table S4 The area of C 1s and Cu 2p from the surface of saline-alkali soils and adsorption Cu, remove organic matter and adsorption Cu after remove organic matter.

	Cu 2p _{1/2}		Cu 2p _{3/2}		C 1s				
	952.3 eV (Cu ⁺)	953.6 eV (Cu ²⁺)	932.1 eV (Cu ⁺)	933.4 eV (Cu ²⁺)	284.6 eV (C- C)	286.1 eV (C- O)	288.1 eV (C=O)	285.0 eV (C- H)	289.0 eV (O=C- O)
Saline- alkali soil	-	-	-	-	3573	1800	-	-	738
Saline- alkali soil adsorption Cu	2523	2958	5046	5916	3003	1329	601	-	-
Organic- free saline- alkali soil	-	-	-	-	2615	753	428	2193	-
Organic- free saline- alkali soil adsorption Cu	104	744	208	933	839	831	2182	2044	-

Table S5 The area of C 1s and Cu 2p from the surface of biogas residue and adsorption Cu.

	Cu 2p _{1/2}		Cu 2p _{3/2}		C 1s				
	952.3 eV (Cu ⁺)	953.6 eV (Cu ²⁺)	932.1 eV (Cu ⁺)	933.4 eV (Cu ²⁺)	284.6 eV (C- C)	285. 7 eV (C- N)	286. 5 eV (C- O)	288.6 eV (- COOH)	288.1 eV (C=O)
Biogas residue	-	-	-	-	6841	1587	1645	307	-
Biogas residue adsorption Cu	570	2173	1141	4345	1009 9	1550	3107	-	693

Table S6 The percentage of SEM-EDS of saline-alkali soils after adsorption Cu.

	C	O	Mg	Al	Si	Ca	Fe	Cu
site1	16.7	34.5	6.4	9.0	13.8	1.7	5.1	12.0
site2	16.0	36.4	10.3	10.5	13.6	0.8	1.1	10.6
site3	12.1	36.0	12.6	4.00	17.2	1.5	3.0	13.8
Mean \pm SD	14.9 \pm 2.0	35.6 \pm 0.8	9.8 \pm 2.5	7.8 \pm 2.8	14.9 \pm 1.6	1.3 \pm 0.4	3.0 \pm 1.6	12.1 \pm 1.3

Table S7 Relative intensity of major absorption packs in saline-alkali soils (Con.) and application of 2% biogas residue for one season (2%×1), two seasons (2%×2), three seasons (2%×3), four seasons (2%×4), five seasons (2%×5).

	3621 cm ⁻¹	3524 cm ⁻¹	3442 cm ⁻¹	3305 cm ⁻¹	2519 cm ⁻¹	1653 cm ⁻¹	1629 cm ⁻¹	1430 cm ⁻¹	1031 cm ⁻¹	778 cm ⁻¹	694 cm ⁻¹
Con.	35.4	47.8	56.5	45.4	51.2	44.5	47.9	35.6	19.2	46.2	58.5
2%×1	41.4	58.8	72.0	54.5	65.5	45.3	47.7	29.1	9.6	34.9	48.3
2%×2	37.0	52.4	65.5	47.0	52.5	45.0	49.3	37.4	20.5	46.1	59.5
2%×3	37.0	59.2	73.4	53.0	62.1	38.0	40.3	23.8	6.3	26.9	39.6
2%×4	46.6	65.9	79.0	60.4	68.3	46.4	48.5	32.8	12.4	37.7	49.6
2%×5	59.6	67.6	75.7	65.0	94.6	57.7	59.6	42.5	18.2	46.8	57.9

Table S8 The area of Cu 3p from the surface of saline-alkali soils (Con.) and application of 2% biogas residue for one season (2%×1), two seasons (2%×2), three seasons (2%×3), four seasons (2%×4), five seasons (2%×5).

	Con.	2%×1	2%×2	2%×3	2%×4	2%×5
Cu 3p _{3/2} 75.0 eV (Cu ⁺)	561	1404	1709	960	902	2465
χ^2	14.7	9.0	11.6	9.3	11.2	13.6

Table S9 Total organic carbon content in saline-alkali soil, organic-free SAS and biogas residue.

Measuring object	Total organic carbon (%)
Saline-alkali soil	14.60 ± 0.19
Organic-free SAS	0.37 ± 0.02
Biogas residue	14.59 ± 0.136

Data represent the Mean ± SE, three replicates for each sample.