The procedure for measuring and calculating point of zero net charge (PZNC), anion exchange capacity (AEC), and cation exchange capacity (CEC).

A KCl electrolyte (0.01 mol L^{-1}) was used in this study, in which both K and Cl ions were assumed to be bound by non-specific adsorption. Three steps were involved: (1) preparation of a KCl saturated biochar paste, (2) adjustment of the pH of biochar to a range of pH values under the same ionic strength, (3) displacement of adsorbed K and Cl by 1 mol L^{-1} ammonium nitrate. Details are as follows:

(1) Biochar saturation by KCl:

Three grams of biochar samples were suspended in 30 mL of 1 mol L^{-1} KCl in 50 mL centrifuge tubes and then subjected to end-over-end shaking for 1 h. Following centrifugation, the remaining biochar pastes were suspended in 0.2 mol L^{-1} KCl and 0.01 mol L^{-1} KCl for once and twice, respectively and then centrifuged again. The remaining biochar pastes were transferred to Petri dishes, sealed with paraffin, and stored at 4 ℃. The water content of the biochar paste was measured by oven-drying at 105 ℃ for 24 h.

(2) pH adjustment:

Around 0.15 g of the biochar paste (on a dry weight basis) was transferred to 50 mL pre-weighed centrifuge tubes. Thirty milliliters 0.01 mol L^{-1} KCl, adjusted by 0.1 mol L^{-1} KOH or HCl across an adequate pH range under the same ionic strength, were added to a batch of the tubes. The tubes were shaken for 12 h and then centrifuged. The supernatant was carefully collected a 50 mL bottle and the pH value was measured immediately. The concentrations of K^+ and Cl^- in the supernatant were measured as well. The tubes with biochar and entrained solution (0.01 mol L^{-1} KCl) were weighed to calculate the mass of entrained K and Cl inside the centrifuge tubes.

(3) Displacement of adsorbed K and Cl by ammonium nitrate:

Thirty milliliters 1 mol L^{-1} ammonium nitrate were added to the centrifuge tubes and then shaken for 1 h to displace the adsorbed K and Cl ions. This process was repeated twice. All the supernatants were pooled determined for K$^+$ and Cl$^-$ by a flame photometer and titration respectively.

The adsorption of K and Cl ions by biochar was calculated using the following equation:

$$K \text{ or } Cl = n_K \ (or \ n_{Cl}) - M_{entr}m_K \ (or \ M_{entr}m_{Cl})$$

Where n_K and n_{Cl} were the concentrations of K$^+$ and Cl$^-$ determined in 1.0 mol L^{-1} ammonium nitrate (in step 3). M_{entr} denoted as the mass of entrained solution left in the centrifuge tube before ammonium nitrate replacement (in step 2). m_K or m_{Cl} referred to the concentration of K or Cl ions in the supernatant (in step 2).

The surface positive charge was defined as the adsorption of anions (Cl$^-$), and the surface negative charge was the adsorption of cations (K$^+$). A quadratic model was used for fitting surface charge and pH. Point of zero net charges (PZNC) was defined as the pH that had an equal amount of surface positive and negative charge. Anion exchange capacity (AEC) was defined as the amount of net surface positive charge at pH 3.5. Effective cation exchange capacity (ECEC) was defined as the amount of surface negative charge at biochar's pH (under H$_2$O or 1 mol L^{-1} KCl suspension) and potential cation exchange capacity (PCEC) was defined as the amount of surface negative charge at pH 7.