



## Molecular Structures and Sorption Mechanisms of Biochars as Heterogeneous Carbon Materials

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Surface functional groups such as carboxyl play a vital role in the environmental applications of biochar as a soil amendment. However, the quantification of oxygen-containing groups on a biochar surface still lacks systematical investigation. An integrated method combining chemical and spectroscopic techniques was established to quantitatively identify the chemical states, dissociation constants (pKa), and contents of oxygen-containing groups on dairy manure-derived biochars prepared at 100-700 °C. The dissociation pH of carboxyl groups on the biochar surface covered a wide range of pH values (pH 2-11), due to the varied structural micro-environments and chemical states. For low temperature biochars ( $\leq 350$  °C), carboxyl existed not only as hydrogen-bonded carboxyl and unbonded carboxyl groups but also formed esters at the surface of biochars. The esters consumed OH<sup>-</sup> via saponification in the alkaline pH region and enhanced the dissolution of organic matter from biochars. For high temperature biochars ( $\geq 500$  °C), esters came from carboxyl were almost eliminated via carbonization (ester pyrolysis), while lactones were developed. The surface density of carboxyl groups on biochars decreased sharply with the increase of the biochar-producing temperature, but the total contents of the surface carboxyls for different biochars were comparable (with a difference < 3-fold) as a result of the expanded surface area at high pyrolytic temperatures. Understanding the wide pKa ranges and the abundant contents of carboxyl groups on biochars is a prerequisite to recognition of the multi-functional applications and biogeochemical cycling of biochars. A schematic diagram for the dissociation of acid/base groups on biochar surfaces and their related functions was depicted. The protonated biochars favor inorganic anion adsorption and ionizable organic chemical sorption, while the deprotonated biochars favor cationic nutrient retention, heavy metal immobilization, and the release of dissolved materials. For low temperature biochars (i.e. DM100, DM250 and DM350), the acid/base group dissociation directly controls the pH buffering properties of biochars. The resulting surface charges regulate biochars in nutrient retention, sorption/immobilization of hazardous pollutants and biochar particle dispersing properties. Meanwhile, dissociation of acid/base groups affects carbon and silica biogeochemical cycling by regulating the release of organic matter from the cleavage of esters and dissolution of the Si-containing minerals. For high temperature biochars (i.e. DM500 and DM700), the effect of acid/base dissociation on organic matter dissolution is eliminated, but other functions are similar. CGs are the major acid/base groups on biochar surfaces. In field applications, such abundant CGs are worthy of concern in terms of multiple functions of biochars, such as soil pH adjustment, soil nutrient retention, and toxic metals immobilization.