Supporting Information (SI) on

The Adsorption, Aggregation and Deposition Behaviors of Carbon Dots on Minerals

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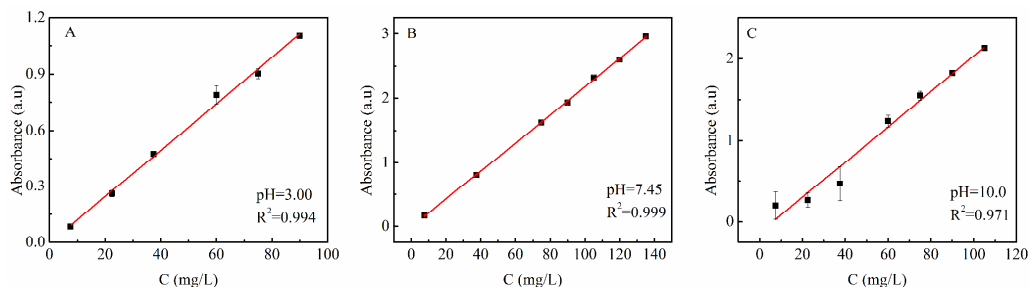
The SI contains 9 pages with 1 Table and 8 Figures.

Figure S1 Calibration curves as absorbance at different conditions versus concentration of CDs. pH=3.00, λ=329.5 nm (A) pH=7.45, λ=333 nm (B) pH=10.0, λ=333.5 nm (C).

Deposition and Transport Experiments. For the deposition experiment, every Teflon-lined screw-cap vial (10 mL) contained 1.0 g/L minerals and 3mL (0.125g/L) CDs, water was used to make the total volume to 6.0 mL. pH 7.45 was chosen because most of subsurface environments are approximately neutral. The mixture was settled for 48 h. For the transport experiment, minerals were dry-packed into borosilicate glass columns (5.0cm×1.5cm) with 5 μm filter membranes. Approximately 0.1 g minerals (dry-weight) were filled to column and then 1.0 mL CDs (0.125g/L) was added slowly. Different columns have different kinds of minerals. Samples 1, 2, 3 and 4 represent kaolinite, montmorillonite attapulgite and goethite, respectively. To simulate the natural environment, the columns were settled down until no CDs dropped down. The intensity of CDs after deposition and transport experiments were determined by UV-vis spectrophotometer.

Dissolution of Minerals. Briefly, 6 mL minerals (2.0 g/L) were added into vials and adjusted pH to 3.00, 7.45 and 10.0. After shaking for 24h, the mineral suspensions were centrifuged (9000 rpm, 10 min) and filtered through polyethersulfone membrane

(0.22 µm). Concentrations of metal ions in filtrates were determined using inductively coupled plasma (ICP-6300, Thermo Fisher Scientific). The results were shown in Figure S2. The concentration of Fe^{3+} released from goethite at pH 10.0 is 0.0058 mM, which is the highest among the three pH values (3.00, 7.45 and 10.0) while no Fe^{3+} was not detected at pH 7.45. The concentation of Al^{3+} released from montmorillonite and kaolinite, 0.02 mM and 0.037 mM, is higher at pH 3.00 than that at pH 7.45 and 10.0. The concentation of Mg^{2+} released from attapulgite is also highest (0.2 mM) at pH 3.00. According to the Schulz-Hardy rule, the critical coagulation concentrations (CCC) of divalent cation is range from 0.5 to 2.0 mM (above 0.2 mM), the tervalent cation is during 0.05-0.1. Therefore, the effect of low concentration of released metal ions from minerals on CDs detection and aggregation was negligible.

pH values of the mineral suspensions (2g/L) were adjusted to 3.00, 7.45 and 10.0, then the tubes were placed in an oscillator and shaken for 24 h. After that the mineral suspensions were centrifuged (9000 rpm, 10 min) and filtered through a Teflon membrane (0.22 um). Supernatant was put into CDs suspensioin at pH 3.00, 7.45 and 10.0. The mixture solution was determined by UV-vis spectrophotometer. Purity CDs solution at same pH and concentration were also determined. The results (Figure S3) showed that the absorbance and spectrum of CDs-Minerals were almost same with CDs aqueous. Thus it indicated the release of metal ions from minerals did not disturb the detection of CDs concentrations (Figure S3).
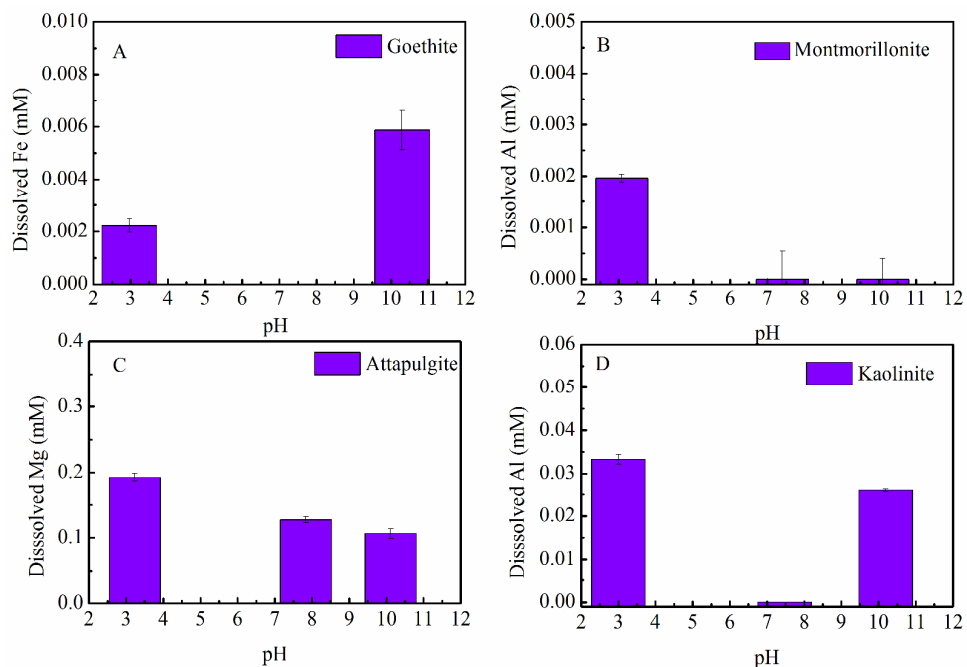
Figure S2 Concentration of dissolved metal ions in mineral suspensions as a function of solution pH values. The mineral suspensions (2g/L) after shaking were centrifuged (9000 rpm, 10 min) and filtered (0.22 μm), then concentrations of metal ions in supernatants were determined using ICP. Concentration of dissolved Fe ions in goethite (A), concentration of dissolved Al ions in montmorillonite (B), concentration of dissolved Mg ions in attapulgite (C), concentration of dissolved Al ions in kaolinite (D).
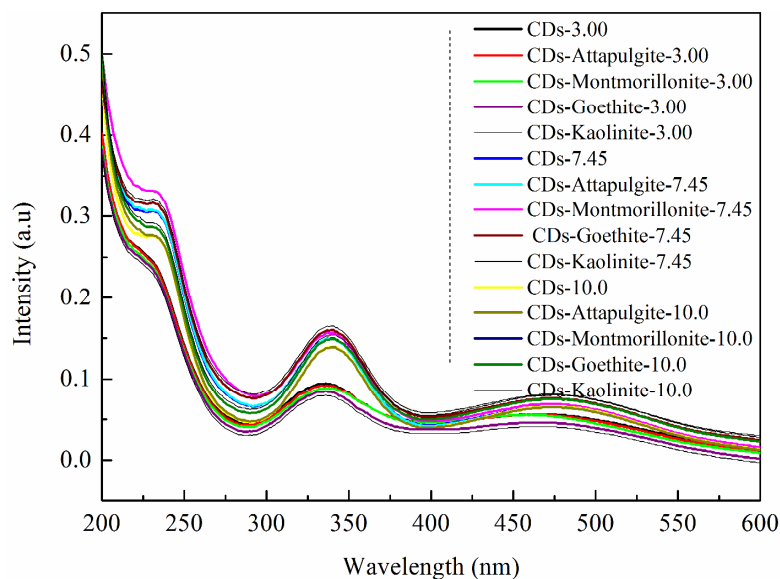
Figure S3 UV-vis absorption spectra of purity CDs (37.5 mg/L) at pH 3.00, 7.45 and 10.0, and the mixed solution of supernatant from minerals (2.0 g/L) and CDs (37.5 mg/L) at pH 3.00, 7.45 and 10.0.
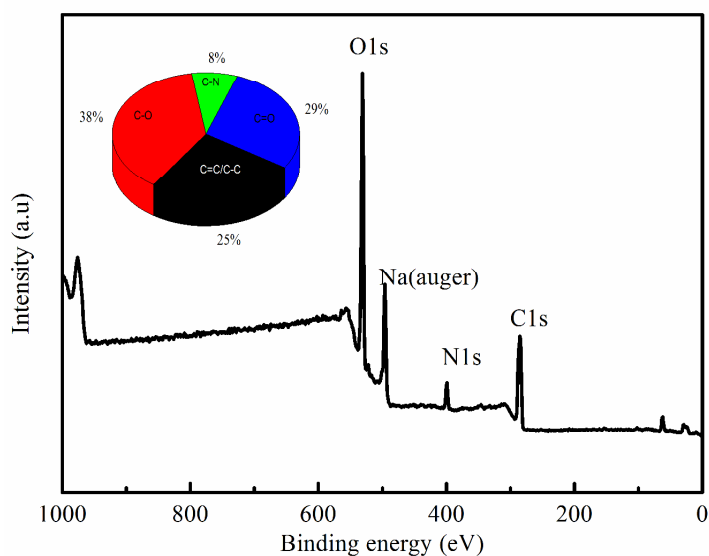

Figure S4 XPS spectrum for CDs. Insert picture is the content of functional groups in CDs got by XPS deconvolution.
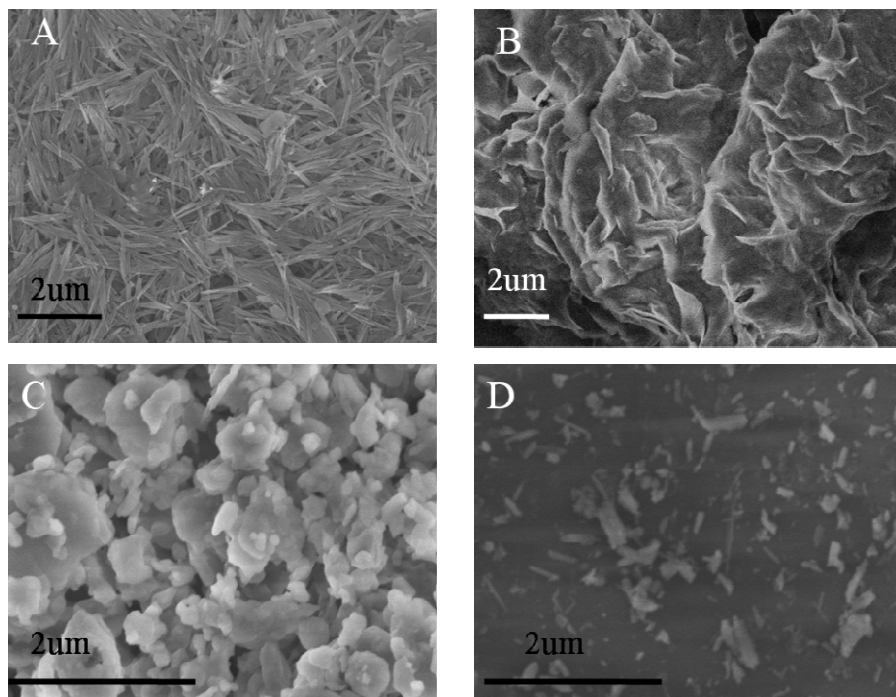
Figure S5 SEM images of attapulgite(A), montmorillonite(B), kaolinite(C), and goethite (D).

Stability of CDs. Possible influencing factors, such as the contact time, CDs concentration and pH value, were examined for the stabilities of CDs under environmental conditions. For the contact time, weak UV-vis absorbance were detected at a contact time 1140 min, as shown in Figure S6A, indicating independent stabilities of CDs with contact time. Similar results were obtained for the concentration effects, as depicted in Figure S6B.
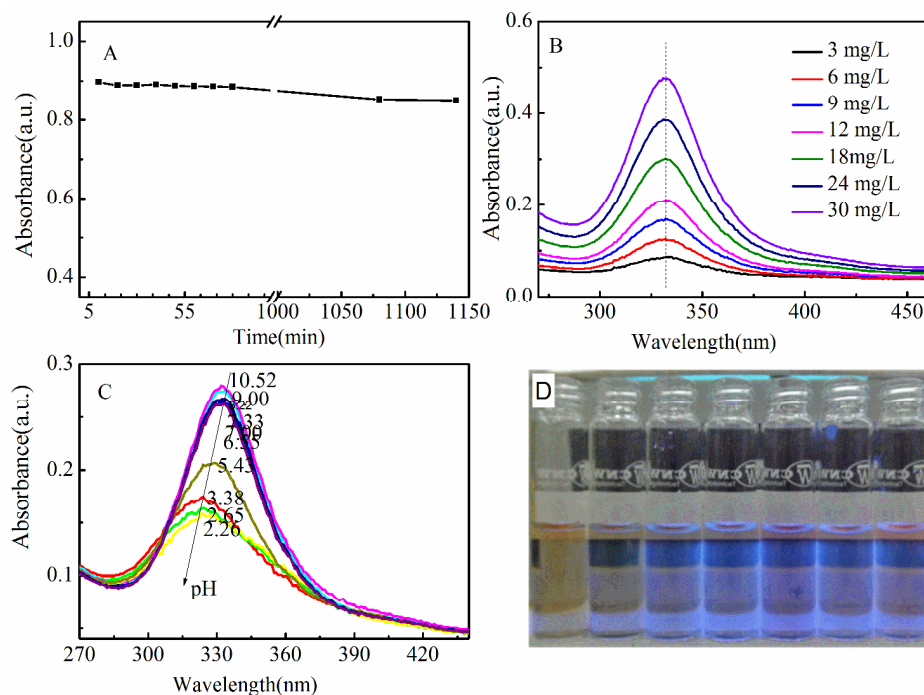
Figure S6 The stability of CDs in aqueous. UV-vis absorbance at λ=333 nm for CDs over time. CDs concentration is 45 mg/L (A) UV-vis spectrum of various concentration CDs range from 3.0 mg/L to 30 mg/L (B) UV-vis spectra of CDs at various pH (C) photographs for CDs solution at various pH (from left to right is 2.26, 3.38, 5.43, 6.55, 7.33, 9.00 and 10.52) taken under 365 nm UV light.
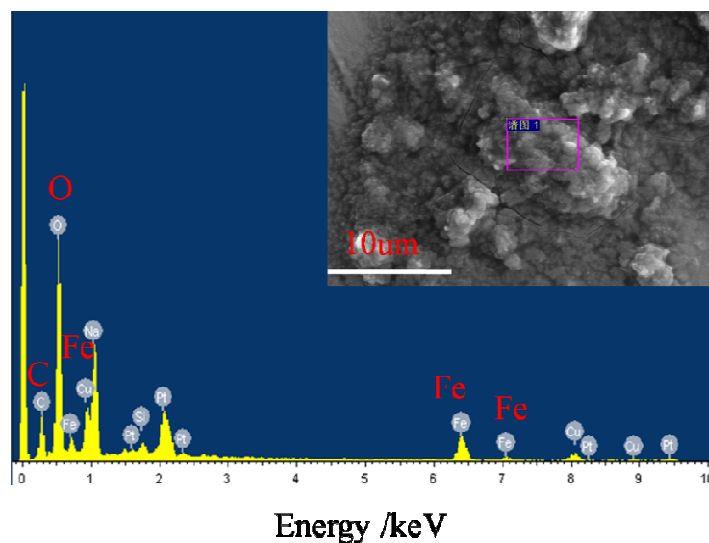

Figure S7 Morphology of CDs−Goethite characterized by SEM. SEM-EDS of

goethite after adsorption of CDs, C_{CDs}=37.5 mg/L, $C_{goethite}$=0.25g/L, the insert picture is the SEM after adsorption.
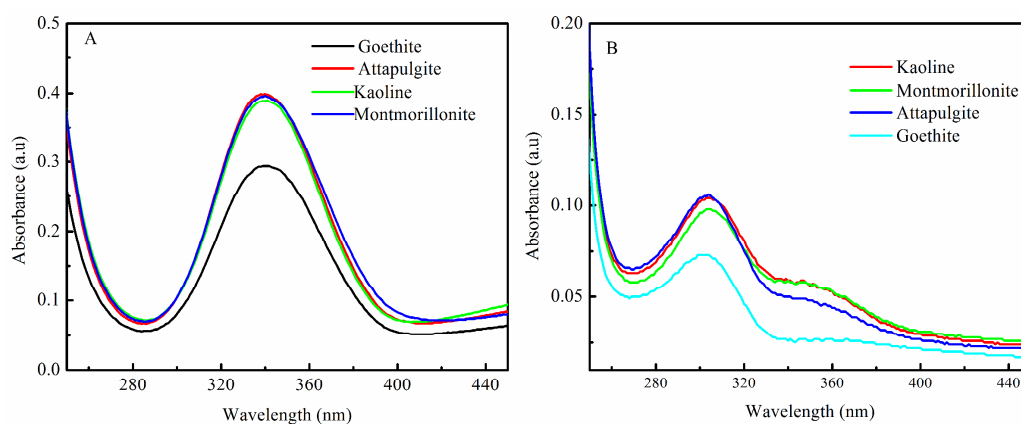

Figure S8 UV-vis absorption spectrum of CDs after deposition and transport in goethite, attapulgite, kaolinite and montmorillonite. The mineral concentration in every Teflon-lined screw-cap vials was 1.0g/L, the concentration of CDs is 0.125 g/L, pH 7.45 (A) The mass of minerals is 0.1g for every column, volume of CDs is 1.0 mL, concentration of CDs is 0.125 g/L (B)

Table1 Parameters for Linear, Langmuir and Freundlich model

Model pH	Linear model		Langmuir model			Freundlich model		
	K	R^2	q_{max} (mg/g)	b(L/g)	R^2	k_F(mg^{1-n} L^n/g)	n	R^2
3.00	0.15	0.95	167.2	0.0023	0.92	1.51	0.65	0.95
7.45	0.005	0.89	30.1	2.3×10^{-6}	0.80	0.39	0.53	0.87
10.0	0.017	0.84	10.3	6.7×10^{-7}	0.75	0.0016	0.35	0.78