

Formation and stability of HA-Fe/Mn colloids in saturated porous media

Junhao Zheng ¹, Mei Jiang ¹, Qingzhu Li ^{1,2} and Weichun Yang ^{1,2,*}

¹ School of Metallurgy and Environment, Central South University, Changsha 410083, China; 203501048@csu.edu.cn (J.Z.); 233512175@csu.edu.cn (M.J.); qingzhuli@csu.edu.cn (Q.L.)

² Chinese National Engineering Research Center for Control and Treatment of Heavy Metal Pollution

* Correspondence: yang220@csu.edu.cn

Text S1

The distribution characteristics of soluble organic matter in HA were further investigated using EEM fluorescence measurements (Fig. S1). The results revealed that HA primarily consists of three main components, namely aromatic proteins, humic acids, and soluble states[1]. The discovery confirmed the presence of predominant active components in HA that closely resemble humic acid, thereby emphasizing its representative qualities as a form of humic acid.

Text S2

The determination of soil organic matter and soil organic carbon followed the heating method of potassium dichromate-sulphuric acid (NY/T 1121.6-2006). The determination of water-soluble OC, Fe, and Mn was carried out by adding 5 g of the soil sample to be tested and 25 ml of distilled water (w/w, 1:5) to the centrifuge tube. The tube was then placed in a shaker and shaken for 30 minutes at room temperature with a speed of 30 rpm. After shaking, the tube was centrifuged for 10 minutes at 3000 rpm, and the supernatant was filtered to determine the content of water-soluble Fe/Mn by ICP-OES, and the content of water-soluble OC by Total Organic Carbon Analyser.

Text S3

The aggregation kinetics of synthesized HA-Fe/Mn colloids were assessed in the present study using the Time-Resolved DLS technique for dynamic light scattering. In this study, we conducted a comprehensive analysis of the aggregation behavior of HA-Fe/Mn colloids by continuously monitoring their z-mean hydrodynamic diameters during the initial phase for a duration of 20 minutes under varying electrolyte concentrations. The aggregation kinetics of HA-Fe/Mn colloids are initiated by the introduction of electrolytes containing divalent cations (Ca²⁺ and Mg²⁺), which induce particle aggregation. The selection of Ca²⁺ and Mg²⁺ is based on their natural abundance and extensive utilization as representative divalent cations in previous studies [2]. To conduct each measurement, approximately 1.5 ml of HA-Fe/Mn colloidal suspension was transferred into a polystyrene cuvette with a specific molar C:Fe/Mn ratio. Then, an appropriate amount of electrolyte stock solution was quickly added to the cuvette to achieve the desired electrolyte concentration. The cuvette (with a total volume of 1.5 mL) was vigorously mixed before being immediately placed into the DLS chamber. The hydrodynamic

diameter (D_h) was monitored every 15 seconds for a duration of 20 minutes. Control experiments were performed using HA alone at a carbon concentration of 10 mg/L, following the same procedure and range of electrolyte concentrations.

The early-stage aggregation rate constant (k) of HA-Fe/Mn colloids was determined by measuring the temporal increase in D_h [3].

$$k \propto \frac{1}{N_0} \left(\frac{dD_h(t)}{dt} \right)_{t \rightarrow 0} \quad (1)$$

The initial concentration of particles in the suspension (N_0) is used to analyze the initial slope ($dD_h(t)_{t \rightarrow 0}$) through linear least squares regression, with increasing D_h until $dD_h(t)$ reaches 1.5 times $dD_h(0)$. The initial aggregation rate constant (k), at a given electrolyte concentration, is normalized to the diffusion-limited aggregation rate constant (α) under non-repulsive and fast conditions (k_{fast}). This normalization is achieved by dividing the initial aggregation rate constant (k) by k_{fast} . Assuming N_0 remains constant in each aggregation experiment, α can be determined as the ratio of the initial slope under reaction-limited conditions to that under diffusion-limited conditions.

The attachment efficiency (α) was determined by normalizing the initial aggregation rate constant obtained at a specific electrolyte concentration (k) to the rate constant acquired under diffusion-limited (non-repulsive, fast) aggregation conditions (k_{fast}) [2].

$$\alpha = \frac{k}{k_{fast}} = \frac{\frac{1}{N_0} \left(\frac{d}{dt} D_h(t) \right)_{t \rightarrow 0}}{\frac{1}{N_{0,fast}} \left(\frac{d}{dt} D_h(t) \right)_{t \rightarrow 0,fast}} \quad (2)$$

Text S4

The deposition of HA-Fe/Mn colloids onto silica interfaces was assessed using a quartz crystal microbalance with dissipation monitoring (Q-Sense E4, Biolin Scientific), which was equipped with four flow modules. The silica surface was chosen as a model because it possesses the properties of quartz sand, simulating the actual environmental surface. The solution was stabilized at room temperature ($23.00 \pm 0.02^\circ\text{C}$) and the laminar flow rate was maintained at 0.1 mL/min using a peristaltic pump (Ismatec SA, Sweden). Prior to the QCM-D experiment, a HEPES/NaCl/pH7 solution was introduced into the chamber until a stable baseline was established. Subsequently, HA-Fe/Mn colloidal suspensions with varying C:Fe/Mn molar ratios were introduced for 20 minutes to achieve deposition. The suspensions is introduced in a process that occurs under continuous stirring conditions. When the HA-Fe/Mn colloid is deposited onto the silica sensor, the resulting mass change of the crystal exhibits a linear proportionality to the frequency, as described by the Sauerbrey relationship [4] (eq 3).

$$\Delta m = -\frac{c}{n} \Delta f_n \quad (3)$$

Where Δm (ng/cm²) represents the mass deposited, n denotes the number of resonant overtones (1, 3, 5, 7, 9, etc.), c signifies the crystal constant (17.7 ng/(Hz·cm²)), and Δf_n (Hz) indicates the frequency shift of the n th overtone.

The deposition attachment efficiency (α_D) is determined by normalizing the deposition rate of the same colloid on a positively charged surface (favorable deposition) [5].

$$\alpha_D = \frac{r_d}{(r_d)_{fav}} = \frac{d\Delta f_3/dt}{(d\Delta f_3/dt)_{fav}} \quad (4)$$

75 In Eq 4, where $\Delta f_3 = \Delta f_{3/3}$, the denominator $(d\Delta f_3/dt)$ fav represents the frequency or dissipation
76 shift rate obtained under optimal conditions, wherein the nanoparticles exhibit opposite
77 charges to that of the QCM-D sensor surface, thereby governing deposition through
78 electrostatic attraction.

Table S1. Summary of Batch HA–Fe/Mn Colloid Formation Experiments.

Expt	Initia Fe mg/L	Initia Mn mg/L	Initia HA mg C/L	Initia molar C/Fe–Mn	Initia molar Fe/Mn	NaCl mM	pH
1	0	0	10	–	–	5	7
2	8	2.6	1	0.4	3	5	7
3	8	2.6	3	1.3	3	5	7
4	8	2.6	5	2.2	3	5	7
5	8	2.6	10	4.3	3	5	7
6	8	2.6	25	10.8	3	5	7
7	8	2.6	50	21.5	3	5	7

Note. Results of batch HA–Fe/Mn colloids formation experiments 1–7 are averages of at least triplicate experiments.

Table S2. The main physicochemical properties.

ITEMS		UNIT	VALUES
organic matter		g/kg	16.1
organic carbon (OC)		g/kg	9.3
Water-soluble	OC	mg/kg	35.2±6.6
	Fe	mg/kg	7.4±2.3
	Mn	mg/kg	2.1±1.6

Table S3. Range distribution of fluorescence area integrals for HA.

	Area	Ex (nm)	Em (nm)	Type
HA	I	350–450	200–275	Humic acid-like
	II	300–375	255–300	soluble microbial byproduct-like

Note. Before EEM measurements, samples with UV absorbance >0.1 at 254 nm need to be diluted with milli-Q water to avoid internal filtering effects.

Table S4. Particle size distribution of HA-Fe/Mn suspensions.

Type	C/Fe–Mn molar	<1-3 nm mg/ CL	1-3~450 nm mg/ CL	> 450 nm mg/ CL
HA	0.4	0.18±0.01	0.57±0.04	8.93±0.01
	1.3	0.31±0.03	2.49±0.22	0.00
	2.2	0.55±0.05	4.19±0.10	0.00
	4.3	1.26±0.01	8.01±0.73	0.00
	10.8	3.85±0.07	19.43±0.95	0.00
	21.5	5.63±0.19	40.72±2.81	0.00
Fe	–	1.96±0.28	0.00	6.04±0.37
	0.4	1.65±0.09	2.49±0.11	3.86±0.55
	1.3	0.45±0.08	5.59±0.04	1.97±0.46
	2.2	0.71±0.01	6.26±0.05	1.03±0.08
	4.3	1.00±0.05	6.58±0.06	0.43±0.03
	10.8	1.00±0.09	6.83±0.36	0.17±0.07
	21.5	1.20±0.09	6.77±0.30	0.04±0.03
Mn	–	1.21±0.06	0.00	1.39±0.14
	0.4	0.66±0.01	0.26±0.02	1.68±0.14
	1.3	0.33±0.01	0.46±0.01	1.81±0.19
	2.2	0.12±0.03	0.65±0.12	1.83±0.09

4.3	0.08 ± 0.02	0.90 ± 0.11	1.61 ± 0.04
10.8	0.04 ± 0.01	1.04 ± 0.15	1.52 ± 0.01
21.5	0.01 ± 0.01	1.17 ± 0.02	1.42 ± 0.00

87

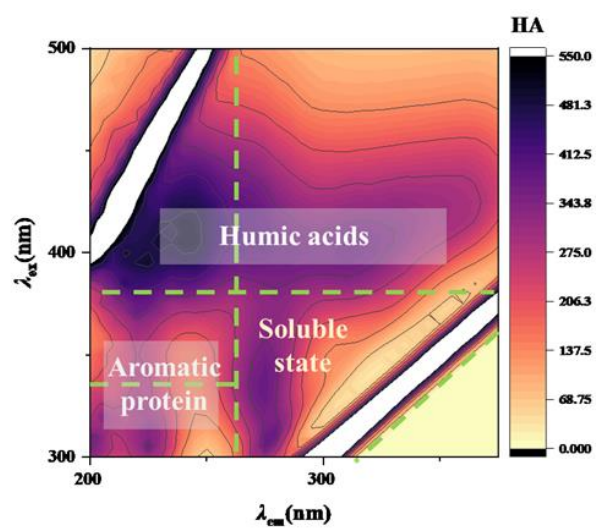


Fig.S1 3D fluorescence spectrum of HA.

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