Supporting information

Rheological behavior of xanthan gum suspensions with Fe-based nanoparticle: the effect of nanoparticle and the mechanism

Weiyong Zhan¹, Hua Zhong^{1, 2, *}, Guansheng Liu^{1, *}, Xianli Liu³

¹ State Key Laboratory of Water Resources Engineering and Management, Wuhan University,

Wuhan 430072, China

² Eastern Institute for Advanced Study, Ningbo 315200, China

³ School of Environmental Science and Engineering, Hubei Polytechnic University, Huangshi 435003, China

* Corresponding author E-mail: zhonghua21cn@126.com (Hua Zhong); gsliu0615@163.com (Guansheng Liu)



Figure S1. Effects of XG concentration on (a) sedimentation and (b) aggregation for nFe_3O_4 in AGW solution.



Figure S2. Sedimentation curves of highly concentrated Fe-based nanoparticles in XG solutions at the concentration of 2.0 g/L. (a) nFe_3O_4 , and (b) nZVI.

Text S1. Sedimentation Experiment with XG Solution.

Sedimentation experiments were firstly implemented to study the effect of XG on the stability of the nanoparticle suspension at relatively low particle concentrations (i.e., 0.2 g/L). The nFe₃O₄-XG suspensions were prepared by dispersing nFe₃O₄ in XG solution of predetermined concentrations (i.e., 1.0 g/L and 2.0 g/L), followed by strong shaking and then 30-minute sonication. Then the suspension was transferred into standard cuvette with Teflon stopper (3.5 mL, UV quartz) and was immediately scanned at 730 nm using a UV-vis spectrophotometer (UV-2600, Shimadzu, Japan) in a drive-time mode for 10 h to examine the settlement kinetics of the nFe₃O₄ in the solution. The wavelength of 730 nm was selected because nFe₃O₄ had the highest absorbance at this wavelength (Figure S1a) and the mass concentration of nFe₃O₄ has a good linear relationship with its absorbance. After converting the absorbance to the mass concentration, sedimentation curves of the normalized concentration, C/C_0 as a function of time were plotted (*C* is the nFe₃O₄ concentration at sampling time *t* and C_0 is the initial concentration.). Moreover, the size of the particles was measured using Nano-ZSP Zetasizer (Malvern Instruments, U.K.) based on the dynamic light scattering mechanism (DLS).



Figure S3. The spectral scanning for nFe_3O_4 in the wavelength range of 185-900 nm.

The stability of the highly concentrated nFe₃O₄ suspension (i.e., 2, 4, 8, 20 g/L) in the XG solution of 2.0 g/L was examined. Because the optical absorbance of the highly concentrated suspension exceeded the top detection limit of linearity of the spectrophotometer, the sedimentation of the particles was examined using another method. In brief, the nFe₃O₄ suspensions was prepared by dispersing nFe₃O₄ in XG solution (2.0 g/L) to produce suspensions containing nFe₃O₄ at concentration of 2, 4, 8, 20 g/L followed by stirring and sonication. The suspensions were then immediately transferred into 250-mL volumetric cylinder. Samples with a size of 0.2 mL were withdrawn at predetermined time intervals at a depth of 5.8 cm below the surface. Each sample was mixed with hydrochloric acid with a water bath at 60 °C for 30 min to achieve complete dissolution of the nFe₃O₄. The total iron concentration in the samples was measured using a HACH DR2800 spectrophotometer (Loveland, CO) using the FerroVer method (procedure No. 8008).¹ Before the measurement, the sample was diluted to set the iron concentration within the detection range of this method. The stability of highly concentrated nZVI was also examined using the same experimental procedure.

Text S2. Sedimentation of Fe-based nanoparticles in XG Solution.

The sedimentation curves of nFe₃O₄ in XG solutions are presented in Figure S1a. For nFe₃O₄ alone at a concentration of 0.2 g/L, C/C_0 decreased from 1.0 to 0.07 after 1.5 h, showing a removal efficiency of 93%. Such a rapid settlement of nFe₃O₄ could be effectively inhibited by XG, especially at a concentration of 2.0 g/L. In the presence of 1 g/L of XG, the removal efficiency of nFe₃O₄ was only 20% after 10 h, which was significantly lower than the control group (93%). At the XG concentration of 2.0 g/L, there was no settling during the whole-time frame of the experiment. Figure S1b presents the influence of XG concentration on particle size of nFe₃O₄. The particle size is more than 600 nm for nFe₃O₄ in the absence of XG. The size is much larger than the size of single particles (~20 nm), which indicates that nFe₃O₄ are highly aggregative. XG significantly reduced the size of nFe₃O₄. When XG concentration was 2.0 g/L, the size of nFe₃O₄ was reduced to approximately 50 nm, and showed no significant change during the period of the tests (12.5 h), indicating stability against aggregation. These results show that a stable dispersal state of the nanoparticles can form at 2.0 g/L of XG.

XG is a long-branched polymer which can form a network structure through entanglement and hydrogen bonding.^{2, 3} This network structure can stabilize the nanoparticles. The particles in the solution can enter and be trapped in the voids within an entangled network.⁴ From a viewpoint of kinetics, the Brownian motion of particles trapped in the voids can be greatly limited, which reduces the probability of particle collisions and aggregation.^{2, 5} To further demonstrate such an entangled network stabilization, the sedimentation of high-concentration of nFe₃O₄ and ZVI nanoparticles are examined and results are shown in Figure S2. The nFe₃O₄ with an initial concentration in the range of 2 to 20 g/L was stabilized by XG at the concentration of 2.0 g/L for the experimental timeframe of 30 days (Figure S2a). Similarly, nZVI at a concentration of 8 g/L was stabilized for 11 days (Figure S2b). The independence of the stability on the concentration of the nanoparticles was consistent with the entangled network stabilization mechanism. In all, these results indicated an entangled network formation in the XG suspension of Fe-based nanoparticle.

Text S3. MAE, RMSE, R² and AIC

The mean absolute error (MAE), the root mean squared error (RMSE), and the determination coefficient (\mathbb{R}^2) are common means of assessing model performance by statistical comparison between the model simulations (y_i , i = 1, 2, ..., x) and experimental observations (Y_i , i = 1, 2, ..., x).⁶ AIC deal with the trade-off between the goodness of fit of the model and the model complexity, in which the penalty term for the number of parameters in the model is introduced.⁷ MAE, RMSE, \mathbb{R}^2 and AIC are defined as follows

$$MAE = \frac{1}{x} \sum_{i=1}^{x} |y_i - Y_i|$$
(S1)

$$RMSE = \sqrt{\frac{1}{x} \sum_{i=1}^{x} (y_i - Y_i)^2}$$
(S2)

$$R^{2} = 1 - \frac{\sum_{i=1}^{x} (y_{i} - \overline{Y}_{i})^{2}}{\sum_{i=1}^{x} (Y_{i} - \overline{Y})^{2}}$$
(S3)

$$AIC = x log \left(\frac{1}{x} \sum_{i=1}^{x} (y_i - Y_i)^2\right) + 2p$$
(S4)

where x represents the total number of the results, y_i is the simulated result of the coupled model and Y_i is the observed result, p is the number of fitting parameters, and subscript *i* represents the serial number of the results.

Reference

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