Supplementary Material Cover Sheet

Comparison of the effects of chemical surfactant and bio-surfactant on montmorillonite colloid-mediated transport of levofloxacin through saturated porous media

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S1. Determination of the ζ-potential of quartz sand

The zeta potential of sand grains was measured using a zeta-plus potential analyzer (Zetasizer nano ZS90, Malvern Instruments, UK) at room temperature (25°C) as described in previous studies [S1, S2]. It should be noted that the size of sand grains was large enough that they were not suitable for direct measurement with a zeta analyzer, so these grains were crushed into a fine powder and mixed with an appropriate solution in an ultrasonic bath for 30 min. Then, the mixture formed into a sufficiently stable suspension that could be used for zeta potential measurement.

S2. Preparation of montmorillonite colloids

Clay colloids were prepared following the procedure provided by Gao et al. [S3]. 10 g montmorillonite were suspended in 200 mL DI water, respectively. After 24 hours of shaking, the suspension was ultrasonicated for 30 minutes and then settled at room temperature for 24 hours. The fraction of colloids in suspension was collected as experimental colloids.

S3. Determination of clay colloid concentrations of the stock solutions

The stock suspensions were quantified by the method of Chotpantarat and Kiatvarangkul [S4]. Briefly, an evaporating dish was heated at approximately 550 °C for 1 h, cooled in an oven for 15-20 min, and then placed in a desiccator until a constant weight was achieved. Next, 100 mL of the clay colloidal suspension was placed in an evaporating dish in a hot air oven at 100 °C overnight and cooled in a desiccator until a constant weight was attained. The gain in weight represented the dry mass of kaolinite or montmorillonite per 100 mL.

S4. Determination of the LEV concentration in the effluent

The LEV concentration in the effluent in each sample was measured after solvent extraction [S5, S6]. Specifically, 3 mL of each sample was taken into 10 mL centrifuge tubes with 0.5 mL 0.25 M NaH_2PO_4 and 0.5 mL acetonitrile. Then, the vials were shaken at 25 °C in the dark for 2 h. Afterward, the samples were sonicated for 45 min to free the antibiotics associated with colloids immediately filtered through 0.1 μm pore size polytetrafluoroethylene membrane for analysis. The concentration of LEV was analyzed directly by using a Waters high-performance liquid chromatography system (HPLC, e2695, Waters Alliance) equipped with a symmetry reversed-phase C18 column (4.6 × 150 mm) using a UV/visible detector at a wavelength of 293 nm.

S5. Adsorption studies of LEV onto montmorillonite colloids in the absence or presence of surfactants

In order to better understand the influences of the different surfactants on the binding affinities of montmorillonite colloids for LEV under experimental conditions, sorption experiments were performed to identify the adsorption capacities of LEV to the colloids with or without surfactants. The experiment was performed by incorporating 30 mg/L of ferrihydrite colloids into 20 mL of a solution containing 1 mg/L of LEV and 1 mM of electrolyte, specifically sodium chloride, within an amber vial under adjusted pH conditions. The mixtures were continuously agitated for a period of 12 h on a rotary shaker maintained at a temperature of 25°C. This duration of agitation was equivalent to the duration of the mobility experiment. Following this, the samples were centrifuged at a rate of 8000 rpm for a period of 10 minutes, after which the liquid fractions were filtered through a 0.22 μm membrane filter to isolate the dissolved LEV (i.e., Ce (mg/L)). The mass of LEV adsorbed to montmorillonite colloids (i.e., q, in mg/g) was determined using the mass balance method.

S6. Adsorption studies of surfactants onto sand

Adsorption experiments studied the adsorption capacity of surfactants on sand under different conditions. First, about 5 grams of sand was weighed and transferred to a 20 milliliter amber glass bottle with 20 mL of solution containing 1 mM of NaCl and 10 mg/L of surfactants (i.e., rhamnolipid or SDBS). The vials were then balanced by horizontal shaking for 12 hours (the duration was equivalent to the transport experiment). In addition, the vials were centrifuged at 8000 rpm for 20 min and the supernatant was extracted.

The concentration of rhamnolipid was determined by the chromogenic method. Rhamnolipid is a kind of glycolipid. The phenol-sulfuric acid method is the most used quantitative method [S7]. That is, 2.00 mL supernatant was poured into the colorimetric tube, each of which was added with 0.05 80% phenol reagent and 5 ml concentrated sulfuric acid. After full oscillation, the solution was boiled in water of 25-30°C for 10-20 min and then cooled to room temperature. To quantify rhamnolipid, the absorbance of each concentration was measured at the wavelength of 480 nm by ultraviolet spectrophotometer and recorded. All absorbance measurements were made using an ultraviolet-visible spectrophotometer (TU-1810PC, Purkinje General, Beijing, China). The concentration of SDBS in the supernatant was also analyzed by the UV/vis spectrophotometer at 223 for SDBS [S8]. The difference between the initial and final concentration of the surfactant in the aqueous phase then determines the adsorbed surfactant. All experiments are in triplicate.

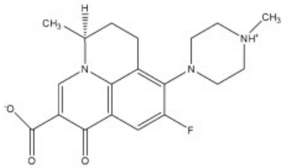
S7. Adsorption of surfactants onto montmorillonite colloids

Adsorption experiments were also conducted to determine the adsorbed amount of surfactants onto montmorillonite colloids under different solution chemistry conditions. The initial concentrations of surfactants in the 20-mL amber glass vial were 10 mg/L, and the initial concentrations of clay colloids were 50 mg/L. The vials were mixed the vials were left on an orbital shaker operated at room temperature for 12 h. The liquid and solid phases were separated by centrifugation at 8000 rpm for 30 min, and then the supernatants were filtered through 0.1 μm filtering membrane. The concentrations of surfactants in supernatants were determined based on the method mentioned in Section S5. The adsorbed surfactant was then determined by the difference between the initial and final phosphate concentrations in the aqueous phase. All experiments were run in triplicate.

Table S1. Selected physicochemical properties of clay minerals tested.

Clay minerals	Chemical composition	Total specific surface area (m^2/g)	pH_{PZC}	Cation-exchange capacity (meq/100g)
Montmorillonite	$(OH)_4Si_8Al_4O_{20}•nH_2O$	49.4	2.7	93

Table S2. Selected properties of levofloxacin.

Antibiotics	Molecular formula	Chemical structure	Molecular weight (g/mol)	pk_a[a]
levofloxacin	$C_{18}H_{20}FN_3O_4$		361.37	pK_{a1}=6.02 pK_{a2}=8.25

[a] Derived from Al-Jabari et al. [S9] .

Table S3. Physical and chemical characteristics of SDBS.

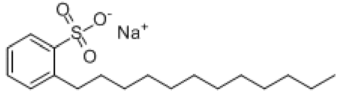
Antibiotic/Surfactant	Abbreviation	Molecular formula	Molecular weight (g/mol)	Molecular structure
Surfactant sodium dodecylbenzene sulfonate	SDBS	$C_{18}H_{29}NaO_3S$	348.5	

Table S4. Adsorption amount of surfactants onto sand. Error bars represent standard deviations from replicate experiments (n=3)

surfactants	electrolyte solution	pH	*q* (mg-surfactant/kg-sand)
10 mg/L Rha	1 mM NaCl	5.0	15.3 ± 1.7
10 mg/L SDBS	1 mM NaCl	5.0	18.1 ± 2.3
10 mg/L Rha	1 mM NaCl	7.0	12.5 ± 0.5
10 mg/L SDBS	1 mM NaCl	7.0	15.7 ± 1.2
10 mg/L Rha	1 mM NaCl	9.0	8.9 ± 0.3
10 mg/L SDBS	1 mM NaCl	9.0	11.6 ± 0.7

Table S5. Adsorption amount of surfactants onto montmorillonite colloid (50 mg/L). Error bars represent standard deviations from replicate experiments (n=3)

surfactants	electrolyte solution	pH	*q* (mg-surfactant /g-colloids)
10 mg/L Rha	1 mM NaCl	5.0	132.3 ± 3.6
10 mg/L SDBS	1 mM NaCl	5.0	156.4 ± 7.2
10 mg/L Rha	1 mM NaCl	7.0	107.6 ± 5.1
10 mg/L SDBS	1 mM NaCl	7.0	139.4 ± 4.5
10 mg/L Rha	1 mM NaCl	7.0	91.7 ± 2.4
10 mg/L SDBS	1 mM NaCl	7.0	108.1 ± 1.3

Table S6. ζ-potentials (mV) of quartz sand under different conditions.

No.	quartz sand	surfactants	electrolyte solution	pH	ζ-potentials (mV)
1	quartz sand	0	1 mM NaCl	5.0	-42.3 ± 0.6
2	quartz sand	10 mg/L Rha	1 mM NaCl	5.0	-45.7 ± 1.0
3	quartz sand	10 mg/L SDBS	1 mM NaCl	5.0	-49.2 ± 0.3
4	quartz sand	0	1 mM NaCl	7.0	-50.2 ± 0.5
5	quartz sand	10 mg/L Rha	1 mM NaCl	7.0	-55.6 ± 0.8
6	quartz sand	10 mg/L SDBS	1 mM NaCl	7.0	-59.3 ± 1.2
7	quartz sand	0	1 mM NaCl	9.0	-55.1 ± 0.2
8	quartz sand	10 mg/L Rha	1 mM NaCl	9.0	-57.6 ± 0.1
9	quartz sand	10 mg/L SDBS	1 mM NaCl	9.0	-59.8 ± 0.7

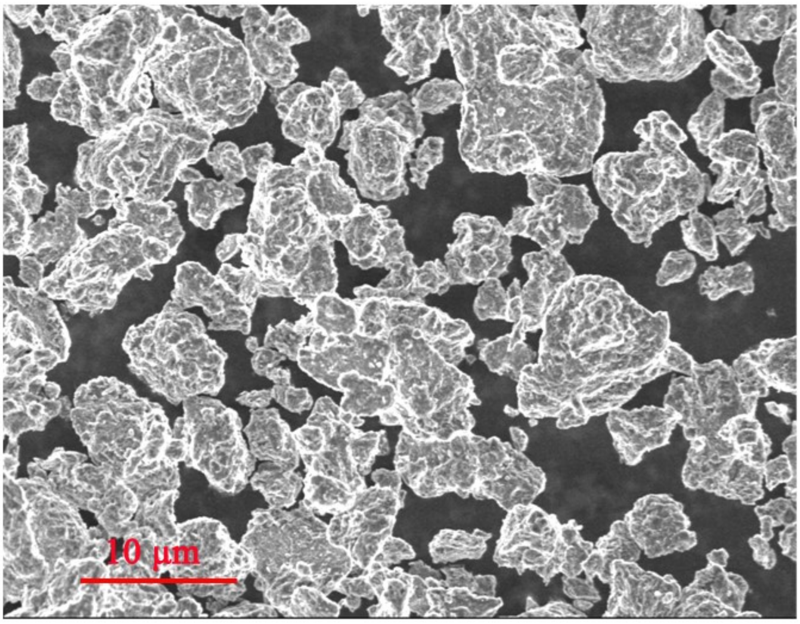
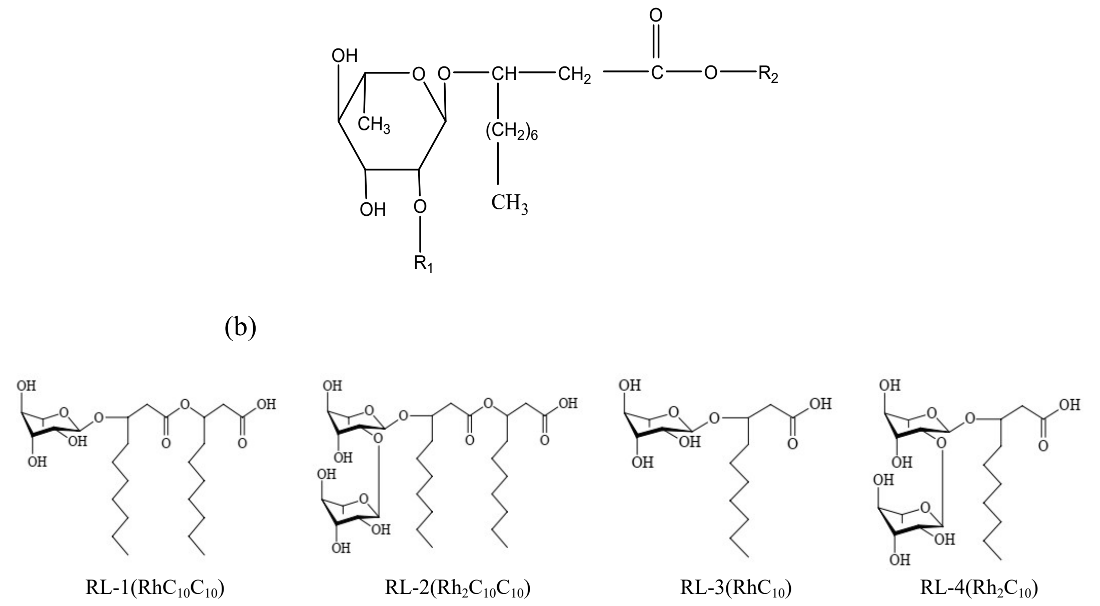


Fig. S1. Representative scanning electron microscope (SEM) images of montmorillonite.



RL-1($RhC_{10}C_{10}$) RL-2($Rh_2C_{10}C_{10}$) RL-3(RhC_{10}) RL-4(Rh_2C_{10})

Fig. S2. Chemical structure of rhamnolipid with general formula [S10]; and (b) four common rhamnoolipid structures. Typically, RL-1($RhC_{10}C_{10}$) and RL-2($Rh_2C_{10}C_{10}$) were considered to be the main rhamnolipidic congeners, having variable relative proportions in mixture (RL respents rhamnoolipid) [S11].

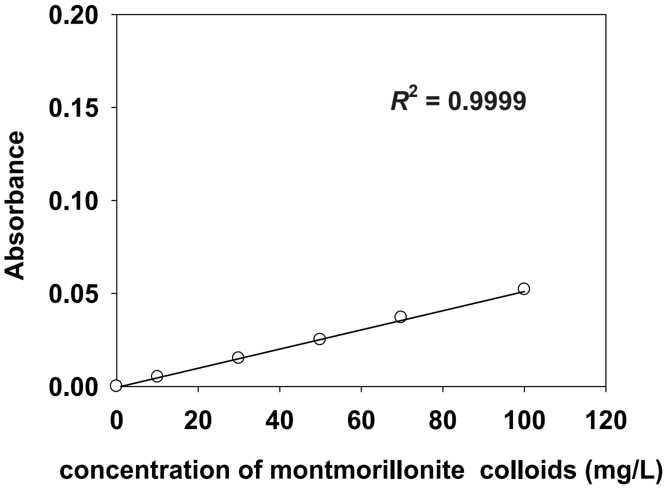


Fig. S3. Calibration curve as absorbance vs. concentration of montmorillonite colloid in suspension (absorbance at the wavelength of 410 nm).

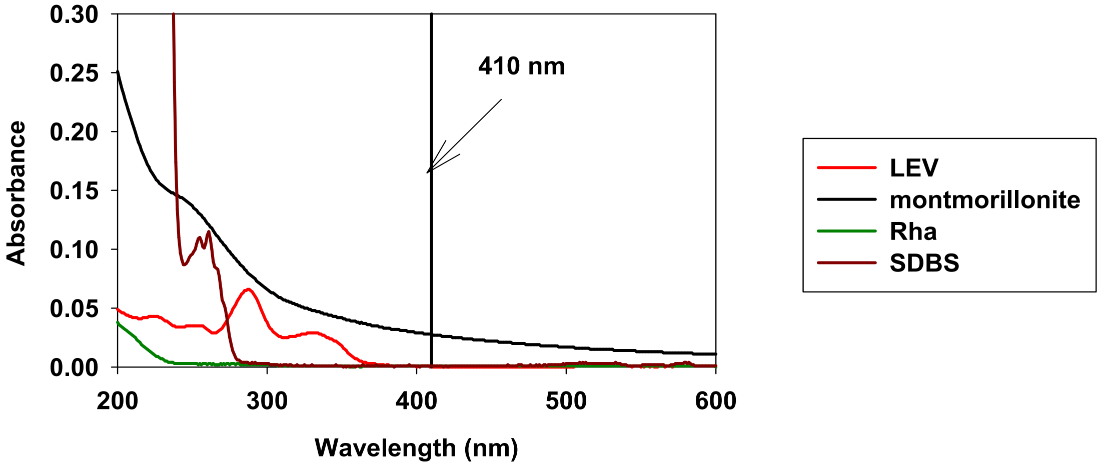


Fig. S4. UV/Vis spectra of LEV (1 mg/L), montmorillonite colloids (50 mg/L), rhamnolipid (10 mg/L), and SDBS (10 mg/L) dispersed in DI water.

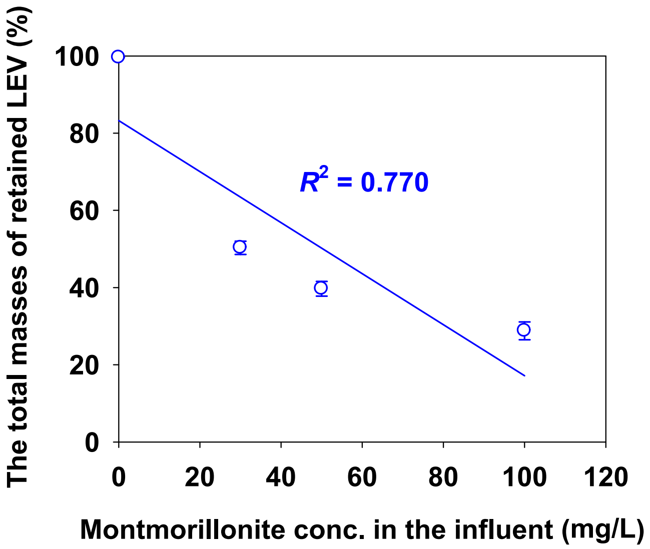
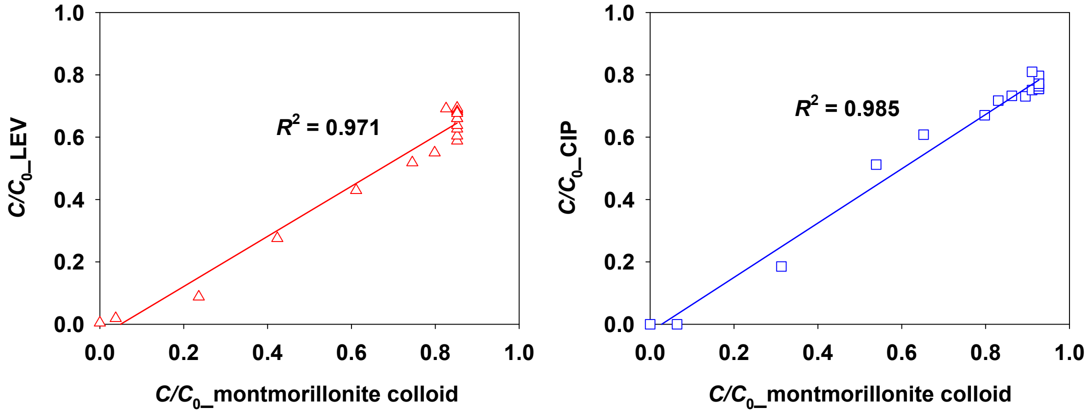


Fig. S5. Comparison between the retained mass of LEV in the columns and concentration of montmorillonite colloids in the influent for columns 1–4.

(a) 30 mg/L (column 2)

(b) 50 mg/L (column 3)



(c) 100 mg/L (column 4)

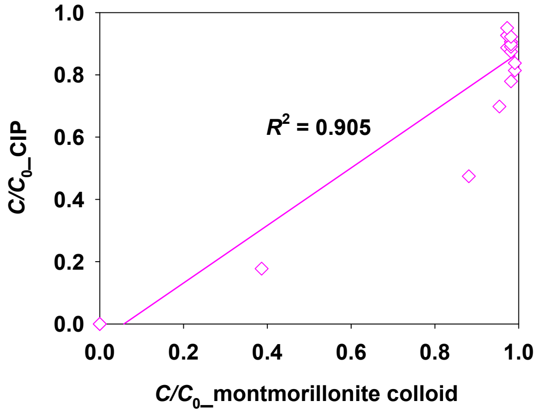


Fig. S6. Comparison of montmorillonite colloids breakthrough and LEV breakthrough in the respective effluent for columns 2–4.

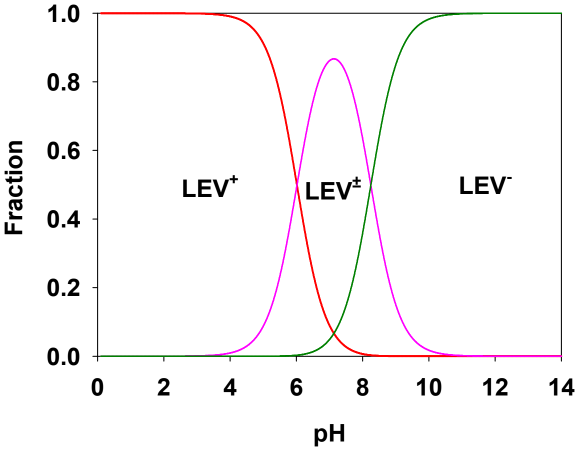


Fig. S7. pH-dependent speciation of the whole LEV molecular and the functional groups.

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