Fullerol-facilitated transport of copper ions in water-saturated porous media: Influencing factors and mechanism

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HIGHLIGHTS

- $C_{60}(OH)_n$ could facilitate the transport of Cu^{2+} in water-saturated porous media.
- The facilitated transport of Cu^{2+} was affected by pH and $C_{60}(OH)_n$ concentration.
- The presence of $C_{60}(OH)_n$ decreased the retention factor of Cu^{2+} .
- The facilitation was mainly due to the higher adsorption of Cu^{2+} by $C_{60}(OH)_n$.

GRAPHICAL ABSTRACT

$C_{60}(OH)_n$ Cu^{2+}

Fullerol-facilitated transport

ARTICLE INFO

Article history:

Received 16 March 2017

Received in revised form 17 June 2017

Accepted 1 July 2017

Available online 3 July 2017

Keywords:

Facilitated transport

Copper ions

Fullerol nanoparticles

Porous media

ABSTRACT

The environmental safety of carbon nanomaterials (CNMs) has become a hot spot of worldwide research work. The high stability, mobility and adsorption capability of CNMs may give rise to the enhancement of heavy metal transport. However, the understanding of facilitated transport of heavy metal ions by CNMs is still limited. In this research, fullerol nanoparticles ($C_{60}(OH)_n$) were used as a typical CNM to investigate its effect on Cu^{2+} transport in the water-saturated porous media. Column experiments showed that $C_{60}(OH)_n$ could facilitate the transport of Cu^{2+} . Meanwhile, flow velocity showed little impact on the facilitated transport while pH and fullerol concentration played an important role. The mechanism of fullerol-facilitated transport of Cu^{2+} was mainly due to the much higher adsorption capacity of $C_{60}(OH)_n$ than that of the porous media. Besides, the existence of $C_{60}(OH)_n$ decreased the adsorption kinetics of Cu^{2+} on the porous media, which led to a decreasing chance for Cu^{2+} to be retained and thus enhanced the transport of Cu^{2+} .

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1. Introduction

With the development of nanotechnology, the application as well as the emission of nanomaterials has increased. Among them, carbon nanomaterials (CNMs), as typical representative model

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compounds for a variety of applications, has been a hotspot of research [1–3]. So far, many studies have been focused on the biotoxicity and biosafety of CNMs in order to assess their environmental risks [4–8]. However, the risks of CNMs in the environment depend not only on their toxicity but also on their environmental behavior including their fate and transport in the environment and their interaction with other environmental contaminants. Therefore, to further understand and more precisely assess the environmental risks of CNMs, it is imperative to study their environmental behavior.

Previous studies have elaborately evaluated the stability and mobility of typical CNMs, e.g. fullerenes, carbon nanotubes (CNTs), graphene and their derivatives [9–13]. During the production and/or utilization process, CNMs could easily obtain high environmental stability by redox reactions and surface complexation, and thus expose and transport for a long distance in environmental media like water, soil and aquifer [14]. Influencing factors such as CNM characteristics [15], pH and ion strength [16], electrolyte type [17], natural organic matters (NOMs) [18] and surfactants [19] on the stability and mobility of CNMs have also been reported. In addition, CNMs have strong adsorption capability for pollutants in the environment, which may affect the fate and transport of these pollutants. Meanwhile, adsorbed contaminants may increase the hazards of CNM itself too [20]. Thus, it is crucial to study the interaction between CNMs and other contaminants, for instance, the effect of CNMs on the transport of other contaminants.

To date, fullerene nanoparticles (nC_{60}) were proved to facilitate the transport of the organic contaminants, e.g. polychlorinated biphenyl (PCB) and phenanthrene, due to the irreversible adsorption and slow desorption kinetics of nC_{60} for PCB/phenanthrene [21]. Furthermore, it was found that complexation with surfactants or NOMs could significantly enhance the fullerene-facilitated transport of PCB and the breakthrough of PCB increased substantially after fullerene being complexed with surfactants or NOMs [22]. However, the understanding of the influence of CNMs on heavy metal transport is still limited.

The high stability, mobility and adsorption capability of CNMs may lead to the potentially facilitated transport of heavy metals, and further reduce the retention capacity of heavy metals of media and increase the mobility of heavy metal contaminants, which should arouse more attention and concern. Numerous studies have been conducted to delineate the adsorption ability of CNMs for heavy metal ions in the aqueous environment. For example, studies proved that CNTs have high adsorption capacities for divalent metal ions such as Cd^{2+} , Cu^{2+} , Ni^{2+} , Pb^{2+} and Zn^{2+} . Besides, the surface oxidation of CNTs remarkably influenced its adsorption capacities for these ions [23]. The mechanism for adsorption of heavy metals on CNMs was mainly the electrostatic attraction, complexation of heavy metal ions with the surface functional groups of CNMs, and the sorption-precipitation [24].

Since the CNMs show a strong adsorption ability for heavy metals, it is reasonable to hypothesize the potentially facilitated transport of heavy metals by CNMs. However, the study on the effect of CNMs on the transport of heavy metals in the porous media is still a lack. Consequently, the primary objective of this research is to study the effect of a typical CNM, i.e., fullerol nanoparticles ($\text{C}_{60}(\text{OH})_n$), on the transport of Cu^{2+} , one of the typical heavy metal ions, in the porous media, in order to improve the understanding of the environmental risks of CNMs. Based on the study of the stability and mobility of $\text{C}_{60}(\text{OH})_n$, whether the average flow velocity, pH, and fullerol concentration would play a role in the potential effect was investigated. Batch adsorption experiments were also conducted to understand the mechanism of the facilitated transport. The results from this study can be regarded as a supplement

to obtain a more reliable assessment of the interaction of CNMs with heavy metal contaminants in the aqueous environment.

2. Experimental

2.1. Materials

Fullerols, which was claimed to have 18–28 hydroxy functional groups by the producer, was purchased from Nanjing XFNANO Materials Tech Co. Ltd (Nanjing, China). It was used as received without further purification. The molecular structure of fullerol was shown in Fig. S1. Quartz sand bought from Beijing Shuangxiangda Instrument Sales Department was used as the porous media. The average particle size of the quartz sand was 523 μm , which was measured by Laser Diffraction Particle Size Analyzer (Mastersizer 2000, Malvern Instruments Ltd., UK). Before being used, the quartz sand was carefully washed with DI water and dried at 80 $^{\circ}\text{C}$ for 12 h.

2.2. Preparation and characterization of fullerol dispersion

$\text{C}_{60}(\text{OH})_n$ dispersion was prepared by weighing a predetermined amount of $\text{C}_{60}(\text{OH})_n$ and adding a prescribed amount of DI water, and then the dispersion was well mixed at 170 rpm under 25 $^{\circ}\text{C}$ for 6 h. The concentration of $\text{C}_{60}(\text{OH})_n$ dispersion was determined using the UV–vis Spectrophotometer (DR5000, Hach Company, US) at 342 nm with matched 10 mm quartz cells. A good correlation between the absorbance and the $\text{C}_{60}(\text{OH})_n$ concentration was observed at this wavelength (Fig. S2).

2.3. Column experiments

Column experiments were employed to investigate the facilitated transport of Cu^{2+} by $\text{C}_{60}(\text{OH})_n$ in the aqueous environment. Each experiment was replicated for three times, which proved that the results were repeatable. The polymethyl methacrylate (PMMA) columns with a height of 12 cm and the inner diameter of 3 cm were employed. Quartz sand was dry-packed into the column at several times. For each time, 1–2 cm height of sand was packed with slight patting on the column side. After that, the porosity of the packed column was measured.

2.3.1. Transport of fullerol nanoparticles

The transport of $\text{C}_{60}(\text{OH})_n$ in porous media under different average flow velocity (12 cm/h and 60 cm/h) and different pH (5.0, 6.7 and 7.8) was investigated. Column porosity of these experiments was found to be 0.37 ± 0.01 . For each experiment, the packed column was firstly loaded with appropriate background solution upward for at least 24 h at the predetermined flow velocity by a peristaltic pump. The background solution was DI water with the same pH of the influent and the pH of all solutions was adjusted by 0.01 M HCl and/or 0.01 M NaOH solution. After that, a certain amount of influent solution was loaded into the column upward. The effluent was collected at fixed intervals by a fraction collector (SBS-100, Shanghai Qingpu-Huxi Instruments Factory, China). $\text{C}_{60}(\text{OH})_n$ concentrations of influent (C_0) and of effluent samples (C) were measured and the C/C_0 values were calculated to plot the breakthrough curve of $\text{C}_{60}(\text{OH})_n$.

2.3.2. Fullerol-facilitated transport experiments

To study the fullerol-facilitated transport of Cu^{2+} , the columns were packed and loaded with appropriate background solution as the same way mentioned above. Table 1 gives the experimental protocols of the experiments.

The inert tracer used in these experiments was Cl^- , which was prepared by diluting high concentration NaCl solution to 30 mg/L Cl^- . When the flow velocity and pH of the column were stable,

Table 1
Experimental protocols of fullerol-facilitated transport experiments and modeling results of the Cu²⁺ breakthrough curves.

Exp. No.	Column properties			Influent properties			Modeling results			
	ρ_b^a	θ^b	v^c	Conc.	Conc.	pH	D	R	β	ω
	g/cm ³		cm/h	Cu ²⁺ mg/L	C ₆₀ (OH) _n mg/L		cm ² /h			
1	1.67	0.37	58.62	9.82		6.7	4.48	15.43	0.60	2.24
2	1.70	0.36	60.36	9.95	101.5	6.7	6.70	8.30	0.24	0.57
3	1.66	0.37	12.36	9.91		6.7	5.46	– ^d	–	–
4	1.63	0.38	11.65	9.70	99.6	6.7	4.61	8.40	0.34	0.42
5	1.68	0.37	59.61	10.26		7.8	5.85	–	–	–
6	1.66	0.37	58.68	10.60	101.7	7.8	4.85	5.42	0.38	0.51
7	1.69	0.36	60.06	10.61		5.0	7.49	23.17	0.44	0.89
8	1.71	0.36	61.80	10.37	100.4	5.0	7.25	15.55	0.19	1.07
9	1.63	0.39	59.19	10.10	50.5	6.7	4.50	4.61	0.58	0.63
10	1.62	0.39	58.62	10.20	31.4	6.7	3.18	12.48	0.23	1.31

^a Bulk density of the column.

^b Porosity of the column.

^c Average flow velocity.

^d Since no Cu²⁺ breakthrough was observed in experiment 3 and 5, the inverse solution method cannot be used to calculate the parameters R , β and ω .

tracer solution with the same pH was loaded upward and the effluent was sampled at fixed intervals. Then the Cl[−] concentration was measured by Ion Chromatography (ICS-1500, Thermo Fisher Scientific Inc., US) and the breakthrough curve of tracer was analyzed for later modeling. After the tracer experiment, the column was flushed with background solution for about 6 h to eliminate the NaCl retained in the column.

Before being input to the column, the influent solution with predetermined Cu²⁺ and C₆₀(OH)_n concentration were mixed at 170 rpm under 25 °C for over 24 h for complete adsorption. After the column being flushed, the influent was input upward and the effluent was collected at fixed intervals. The Cu²⁺ concentration in the influent (C₀) and the effluent samples (C) were analyzed by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) (ICPE-9800, Shimadzu Corporation, Japan) and the C₆₀(OH)_n concentration was measured as mentioned above.

Table 1 Experimental protocols of fullerol-facilitated transport experiments and modeling results of the Cu²⁺ breakthrough curves.

2.4. Modeling

The physical non-equilibrium convective-dispersive equation was used to model the Cu²⁺ transport [25]. In this model, the liquid phase in the porous media was divided into mobile and immobile phases. Solute transport was confined only to the mobile water phase. In the immobile phase, the solute transfer was assumed to be diffusion controlled.

$$\beta R \frac{\partial C_1}{\partial t} + (1 - \beta) R \frac{\partial C_2}{\partial t} = \frac{1}{P} \frac{\partial^2 C_1}{\partial x^2} - \frac{\partial C_1}{\partial x} \quad (1)$$

$$(1 - \beta) R \frac{\partial C_2}{\partial t} = \omega (C_1 - C_2) \quad (2)$$

$$P = vL/D \quad (3)$$

where C_1 , C_2 are the solute concentrations of the mobile and immobile water phase, β is a dimensionless variable which means the distribution of water in the mobile and immobile phase, R is the retardation factor which represents the extent of retention of solute in the porous media, D is the dispersion coefficient (cm²/h) which is obtained from modeling the tracer experiment, v is the average flow velocity (cm/h), L is the transport distance (cm) which equals to the column length in this study, P is Peclet number, t is time and ω is a dimensionless rate constant. The parameters were simulated by STANMOD program using the inverse solution method.

2.5. Batch adsorption experiments

Batch adsorption experiments were conducted to study the mechanism of the facilitated Cu²⁺ transport by C₆₀(OH)_n. In a typical adsorption isotherm experiment, a certain amount of Cu²⁺ solution with predetermined concentration were added into a 50 mL centrifuge tube containing 50 mg/L C₆₀(OH)_n dispersion or 5 g quartz sand. The tube was shaken at 25 °C, 170 rpm for over 24 h and then sampled with an injector. In order to remove C₆₀(OH)_n, samples containing C₆₀(OH)_n were filtered using a 3 KD Millipore Ultrafiltration Device centrifuged at 10,000 rpm for 20 min. Other samples were filtered using a 0.22 μm PES filter. Then the Cu²⁺ concentration was measured to calculate the adsorption amount.

In a typical adsorption kinetics experiment, two glass bottles were used, which contain 500 mL 10 mg/L Cu²⁺ solution, respectively. 50 mg C₆₀(OH)_n was added into one of the bottles and no C₆₀(OH)_n added into another one. The two bottles were shaken at 25 °C, 170 rpm for 24 h for full adsorption. Then 50 g quartz sand was added into each bottle respectively, and the bottles were shaken at 25 °C, 220 rpm. Samples were taken at 0, 5, 10, 30, 60, 120, 240, 520, 1000, and 1500 min respectively and filtered with 0.22 μm PES filters. The Cu²⁺ concentration was measured to calculate the adsorption amount.

3. Results and discussion

3.1. Stability and mobility of fullerol nanoparticles

The aqueous stability of C₆₀(OH)_n dispersion is closely related to its electrokinetic characteristics. **Fig. S3** shows the zeta potential of C₆₀(OH)_n dispersion as a function of pH. It was shown that C₆₀(OH)_n are highly negatively charged and its zeta potential ranges from −24.98 to −37.68 mV in the pH range of 4.16–9.19. Under the near-neutral pH condition, the zeta potential is approximate −30 to −31 mV. In the aqueous environment, zeta potential of nC₆₀ dispersion is from −15.1 to −29.9 mV in the pH range of 4.3–9.1 [10]. Generally, a higher absolute value of zeta potential of a dispersion presents a higher stability in the aqueous environment. This is mainly because that a high zeta potential would provide a high electrostatic repulsion between particles in the liquid phase. Thus the C₆₀(OH)_n may have higher stability than nC₆₀ in the aqueous environment.

The stability of fullerol dispersion was also investigated using sedimentation test. It can be seen from **Fig. S4** that the fullerol dispersion has a considerably high stability since its concentra-

Fig. 1. Breakthrough curves of $C_{60}(OH)_n$ under different average flow velocities and pH.

tion almost did not change for 30 days. This result proves that the fullerol dispersion has a higher mobility than SWNTs modified by SDS of a low concentration [26], oxidized MWNTs [27], and nC₆₀ colloids [10].

Breakthrough curves of $C_{60}(OH)_n$ in porous media under the condition of different average flow velocity and different pH are presented in Fig. 1. It could be concluded that $C_{60}(OH)_n$ have significantly high mobility under all conditions investigated in this research since the C/C_0 value reached over 0.9 within only a few pore volumes (PV).

3.2. Fullerol-facilitated transport of copper ions

The column and influent properties are given in Table 1. The effects of three factors, i.e., average flow velocity, pH and fullerol concentration, were investigated.

3.2.1. Effect of average flow velocity

The effect of average flow velocity on the fullerol-facilitated transport of Cu^{2+} was studied and the results are shown in Fig. 2. Under the condition of both high and low flow velocity, the existence of $C_{60}(OH)_n$ in the influent shows considerable enhancement for Cu^{2+} transport. When there is no $C_{60}(OH)_n$, the breakthrough of Cu^{2+} in the porous media is weak and slow and is significantly influenced by flow velocity. Under the high flow velocity, Cu^{2+} is slightly mobile for the breakthrough curve increases slowly since 8 PV and the C/C_0 value reaches 0.47 at the end of the experiment (over 14 PV). But when the velocity is relatively low, Cu^{2+} doesn't show obvious breakthrough within 14 PV. The slow velocity gives Cu^{2+} sufficient time to contact with the surface of the porous media, thus leads to a larger amount of Cu^{2+} adsorbed on the media surface. However, $C_{60}(OH)_n$ significantly facilitated the Cu^{2+} transport. Under both fast and slow flow velocities, the breakthrough curves of Cu^{2+} show a sharp increase in about 2 PV, and the C/C_0 values reach about 0.78 at the end of over 14 PV. In addition, it is shown in Fig. 2 that the breakthrough of Cu^{2+} and $C_{60}(OH)_n$ happened simultaneously, which can also be proved by the good linear correlation between Cu^{2+} and $C_{60}(OH)_n$ concentration (Fig. S4A, B). This phenomenon proves the hypothesis of this research that the $C_{60}(OH)_n$ could enhance the transport of Cu^{2+} by carrying Cu^{2+} to transport through porous media.

CNMs have been proved to enhance the transport of other nanoparticles. For example, the co-transport of nano-TiO₂ and nC₆₀ was investigated and it was found that nC₆₀ would enhance the

Fig. 2. Breakthrough curves of Cu^{2+} and $C_{60}(OH)_n$ in the fullerol-facilitated transport experiments in different flow velocity. A: about 60 cm/h; B: about 12 cm/h.

transport rate of nano-TiO₂ at pH 7 [28]. Functionalized MWNTs was also presented to enhance nano-TiO₂ transport under certain conditions [29]. In these studies, the main mechanism of the enhanced transport is the competition between nano-TiO₂ and CNMs (nC₆₀ and functionalized MWNTs) for deposition sites. However, this could not be the mechanism of the fullerol-facilitated transport of Cu^{2+} in this study since the $C_{60}(OH)_n$ transport is almost not influenced by the presence of Cu^{2+} while in their research, the transport of CNMs was significantly confined by nano-TiO₂. It was reported that modified SWNTs could enhance the mobility of gold nanospheres (AuNSs) due to the facilitated transport of AuNSs where the highly mobile PA-SWNTs acted as carriers for the AuNSs. The enhanced transport was attributed to the higher electrostatic attraction between AuNSs and PA-SWNTs than that between AuNSs and sand surfaces [30]. This could also be the reason for the fullerol-facilitated transport of Cu^{2+} observed in this study since the highly negative charge of $C_{60}(OH)_n$ could effectively attract the positively charged Cu^{2+} thus may decrease the adsorption of Cu^{2+} on quartz sand. It was found that nC₆₀ nanoparticles could facilitate the transport of organic contaminants such as polychlorinated biphenyl (PCB) and phenanthrene through sandy soil columns. Similar to this study, results showed that breakthrough of PCB with nC₆₀ under two different flow velocities were not significantly different. It was concluded that only nC₆₀-absorbed PCB/phenanthrene can break through the soil column since no breakthrough were found in the single transport

of PCB/phenanthrene [21]. However, in this research, Cu^{2+} still showed some breakthrough from the sand column under high flow velocity. Thus the conclusion obtained from this study should be that the adsorption effect gives $\text{C}_{60}(\text{OH})_n$ great ability to facilitate the transport of Cu^{2+} in porous media and the effect is more significant under the slow flow velocity.

3.2.2. Effect of pH

The effect of pH on the fullerol-facilitated transport of Cu^{2+} was studied and Fig. 3 presents the results. It is seen that fullerol-facilitated transport of Cu^{2+} happened under all three pH conditions. However, different from the $\text{C}_{60}(\text{OH})_n$ transport shown in Fig. 1, in which pH shows no obvious influence, both the single Cu^{2+} transport and fullerol-facilitated Cu^{2+} transport were affected by pH.

Under the weakly alkaline condition, Cu^{2+} transport with $\text{C}_{60}(\text{OH})_n$ is enhanced slightly, with a C/C_0 value of 0.89 at over 14 PV, while its transport without $\text{C}_{60}(\text{OH})_n$ is inhibited and breakthrough of Cu^{2+} is not observed at pH 7.8. By contrast, under the weakly acidic condition, Cu^{2+} transport with $\text{C}_{60}(\text{OH})_n$ decreased considerably at pH 5.0 since the C/C_0 value is only 0.61 after 14 PV, while its transport without $\text{C}_{60}(\text{OH})_n$ is almost the same compared with the neutral condition. One possible explanation is that in the alkaline environment, the dissociation and ionization of surface groups on $\text{C}_{60}(\text{OH})_n$ will become easier, which could increase its adsorption ability for Cu^{2+} and then facilitate Cu^{2+} transport. However, in the acidic environment, $\text{C}_{60}(\text{OH})_n$ dissociation and ionization decreased thus the adsorption ability of $\text{C}_{60}(\text{OH})_n$ weakened. Besides, the extra H^+ in the environment is also beneficial for Cu^{2+} desorption from $\text{C}_{60}(\text{OH})_n$ surface. On the other hand, as is shown in Fig. 3, the transport of $\text{C}_{60}(\text{OH})_n$ is slightly enhanced as pH increased, since the C/C_0 value increased and the breakthrough also happened earlier. Therefore, the fullerol-facilitated transport of Cu^{2+} would be inevitably improved as pH increased.

3.2.3. Effect of fullerol concentration

The effect of $\text{C}_{60}(\text{OH})_n$ concentration on the fullerol-facilitated transport of Cu^{2+} was studied and the results are shown in Fig. 4.

It is surprising to find that the enhancement of Cu^{2+} transport by $\text{C}_{60}(\text{OH})_n$ is not entirely positively related to the concentration. It is shown in Fig. 4(A) that a $\text{C}_{60}(\text{OH})_n$ concentration of 31.4 mg/L has only slight enhancement of Cu^{2+} breakthrough since the C/C_0 value at 14 PV is almost the same as the C/C_0 value of single Cu^{2+} transport. The slight enhancement is reflected by the earlier breakthrough of Cu^{2+} with 31.4 mg/L $\text{C}_{60}(\text{OH})_n$ (starting from 3 PV) than without $\text{C}_{60}(\text{OH})_n$ (starting from 8 PV). When the $\text{C}_{60}(\text{OH})_n$ concentration is 50.5 mg/L, the enhancement of Cu^{2+} transport is the highest with a C/C_0 value of 0.98 at 14 PV. However, when the $\text{C}_{60}(\text{OH})_n$ concentration increased to 101.4 mg/L, the facilitated transport of Cu^{2+} decreases for a little bit. In Fig. 4(B), it is apparent that the breakthrough curves of $\text{C}_{60}(\text{OH})_n$ in corresponding experiments present similar phenomena to Cu^{2+} , where the highest C/C_0 value is found when the $\text{C}_{60}(\text{OH})_n$ concentration is 50.5 mg/L.

It was reported that the increasing nC_{60} concentration gave rise to a significant increase of PCB breakthrough [21]. However, in this research, the increase of $\text{C}_{60}(\text{OH})_n$ concentration not always leads to the increase of facilitated Cu^{2+} breakthrough. It can be seen from our results that, when $\text{C}_{60}(\text{OH})_n$ concentration increases from 50.5 to 101.4 mg/L, the Cu^{2+} breakthrough decreases instead. One possible explanation is that aggregation and deposition of $\text{C}_{60}(\text{OH})_n$ were enhanced at a rather high concentration of 101.4 mg/L. To confirm this, the average particle size (Z_{avg}) of $\text{C}_{60}(\text{OH})_n$ nanoparticles in the influent solution of the fullerol-facilitated transport experiments was measured by dynamic light scattering (Zetasizer Nano ZS, UK, Malvern Instruments Ltd.) It is shown that Z_{avg} of $\text{C}_{60}(\text{OH})_n$ with concentrations of 50.5 mg/L and 101.4 mg/L of $\text{C}_{60}(\text{OH})_n$ in

Fig. 3. Breakthrough curves of Cu^{2+} and $\text{C}_{60}(\text{OH})_n$ in the fullerol-facilitated transport experiments at different pH. A: pH 5.0; B: pH 6.7; C: pH 7.8.

10.2 mg/L Cu^{2+} are 135.3 nm and 344.7 nm, respectively. This result indicates that much higher aggregation occurs at $\text{C}_{60}(\text{OH})_n$ concentration of 101.4 mg/L than that at $\text{C}_{60}(\text{OH})_n$ concentration of 50.5 mg/L. In fact, it can be seen from Fig. 4(B) that the retention of $\text{C}_{60}(\text{OH})_n$ with a concentration of 101.4 mg/L increases indeed compared to that with a concentration of 50.5 mg/L, which indicated that the deposition of $\text{C}_{60}(\text{OH})_n$ increases under this concentration. The higher aggregation together with higher deposition of

Fig. 4. Breakthrough curves of Cu^{2+} (A) and $\text{C}_{60}(\text{OH})_n$ (B) in the fullerol-facilitated transport experiments under different $\text{C}_{60}(\text{OH})_n$ concentration.

$\text{C}_{60}(\text{OH})_n$ under $\text{C}_{60}(\text{OH})_n$ concentration of 101.4 mg/L leads to the decreased breakthrough of Cu^{2+} .

It can be noticed that when $\text{C}_{60}(\text{OH})_n$ concentration decrease from 101.5, 50.5 to 31.4 mg/L, the linear relationship between Cu^{2+} and $\text{C}_{60}(\text{OH})_n$ concentration worsens (**Fig. S4A, E, F**). When the concentration of $\text{C}_{60}(\text{OH})_n$ goes stable, the concentration of Cu^{2+} is still

increasing. This means that under relatively low $\text{C}_{60}(\text{OH})_n$ concentration, the breakthrough of free Cu^{2+} (not absorbed by $\text{C}_{60}(\text{OH})_n$) counts for a part of the total breakthrough of Cu^{2+} . When the $\text{C}_{60}(\text{OH})_n$ concentration is lower, the linear correlation is worse, thus the breakthrough of free Cu^{2+} plays a more important role in the total Cu^{2+} breakthrough.

3.2.4. Modeling results

It can be seen from the fitted curves in **Figs. 2–4** that the experimental data fitted the physical non-equilibrium convective-dispersive equation well. The value of several parameters from modeling results was shown in **Table 1**.

During all these parameters, the retention factor R is the most important one since it directly reflects how hard it is for solutes to transport in porous media. In this research, it is obvious that the existence of $\text{C}_{60}(\text{OH})_n$ decreases the R for Cu^{2+} transport. This means that the existence of $\text{C}_{60}(\text{OH})_n$ makes the Cu^{2+} transport in porous media easier. The modeling results are in good agreement with the experimental results and the smallest R value is 4.61 which was found in experiment 9 (with 50.5 mg/L $\text{C}_{60}(\text{OH})_n$).

3.3. Mechanism study

To further understand the mechanism of fullerol-facilitated Cu^{2+} transport, batch adsorption experiments were conducted. **Fig. 5** shows the Langmuir adsorption isotherms of $\text{C}_{60}(\text{OH})_n$ and porous media (quartz sand) on Cu^{2+} :

$$Q = \frac{kCQ_m}{1 + kC} \quad (4)$$

where

Q , Q_m are the adsorption amount and the maximum adsorption capability (mg/g),

C is the equilibrium concentration (mg/L), and

k is the Langmuir adsorption equilibrium constant, generally, the higher k value indicated a higher adsorption ability of the adsorbents.

For $\text{C}_{60}(\text{OH})_n$, the maximum adsorption capability is very high with a value of 222.22 mg/g, and the adsorption equilibrium constant is 1.6071. However, both the two parameters of the porous media have lower values than those of $\text{C}_{60}(\text{OH})_n$. The maximum adsorption capability is only 0.0911 mg/g and the adsorption equilibrium constant is 0.8828. These results show that the $\text{C}_{60}(\text{OH})_n$ have higher adsorption ability on Cu^{2+} than the porous media, which means the Cu^{2+} will be more easily adsorbed by $\text{C}_{60}(\text{OH})_n$

Fig. 5. Langmuir adsorption isotherms of $\text{C}_{60}(\text{OH})_n$ (A) and porous media (B) on Cu^{2+} .

Fig. 6. Effect of $C_{60}(OH)_n$ on the adsorption kinetics of porous media on Cu^{2+} .

other than by the porous media. Therefore, Cu^{2+} could be carried by $C_{60}(OH)_n$ to transport through the porous media.

The effect of $C_{60}(OH)_n$ on the adsorption kinetics of porous media on Cu^{2+} is shown in Fig. 6. Under the two conditions (with and without $C_{60}(OH)_n$), the adsorption kinetics of Cu^{2+} on porous media are in accordance with the pseudo-first-order rate equation:

$$Q_t = Q_e (1 - e^{-kt}) \quad (7)$$

where

Q_t is the adsorption amount at t time (mg/g),

Q_e is the maximum adsorption capacity (mg/g), and

k is the pseudo-first-order rate constant.

The maximum adsorption capacity of the porous media for Cu^{2+} slightly decreased from 0.1119 mg/g to 0.1075 mg/g while the rate constant k also decreases from 0.0067 to 0.0028 with the existence of $C_{60}(OH)_n$. It means that with the existence of $C_{60}(OH)_n$, the rate of Cu^{2+} adsorption by quartz sand decreases, which implies more time and chance for Cu^{2+} to transport through the media and then gives rise to the higher mobility of Cu^{2+} . Thus, the existence of $C_{60}(OH)_n$ can enhance the transport of Cu^{2+} in porous media.

4. Conclusions

In this research, the facilitated transport of Cu^{2+} by $C_{60}(OH)_n$ were investigated based on the study of the stability and mobility of the $C_{60}(OH)_n$ dispersion. The following can be concluded.

- (1) $C_{60}(OH)_n$ dispersion had a relatively high stability and mobility in the aqueous environment.
- (2) Facilitated transport of Cu^{2+} by $C_{60}(OH)_n$ were observed. In addition, flow velocity did not remarkably affect the fullerol-facilitated transport of Cu^{2+} while pH and $C_{60}(OH)_n$ concentration influenced it significantly. The breakthrough of Cu^{2+} fitted the physical non-equilibrium convective-dispersive equation well. Modeling results showed that the presence of $C_{60}(OH)_n$ decreased the retention factor of Cu^{2+} .
- (3) The mechanism of $C_{60}(OH)_n$ to facilitate the transport of Cu^{2+} was mainly due to its much higher adsorption capacity than the porous media. Besides, the existence of $C_{60}(OH)_n$ decreased the adsorption kinetics of the porous media on Cu^{2+} , which led to a decreasing chance for Cu^{2+} to be retained and thus enhanced the transport of Cu^{2+} .

Acknowledgement

This work was supported by the National Natural Science Foundation of China (No. 41473113, 41641034).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhazmat.2017.07.001>.

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