

Influence of SiO₂ Sol and Fe(OH)₃ Colloid on Adsorption Distribution of Benzene Hexachlorides in Groundwater

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Colloid is one of the important factors to affect the migration and transformation of organic pollutants in soil. Take SiO₂ sol and Fe(OH)₃ as the study objects, the adsorption characteristics of BHC with SiO₂ sol and Fe(OH)₃ colloid in the groundwater were studied. The results showed that with the existence of colloid, the order of distribution coefficients for benzene hexachlorides (BHCs) in true solution phase, colloid phase and suspended solids phase in the system from low to high was as follows: $BHC_{S_{SiO_2 \text{ colloid phase}}} > BHC_{S_{\text{suspended solids phase}}} > BHC_{S_{\text{true solution phase}}} > BHC_{S_{Fe(OH)_3 \text{ colloid phase}}} > BHC_{S_{\text{true solution phase}}} > BHC_{S_{\text{suspended solids phase}}}$; the adsorption models of benzene hexachlorides with SiO₂ sol and Fe(OH)₃ colloid were consistent with Henry's isothermal adsorption mode and showing good linear correlation. The adsorption mechanisms of benzene hexachlorides with SiO₂ sol and Fe(OH)₃ colloid were studied by determining the ultraviolet spectrum and the changes in the granularity of the colloid. The result showed that the adsorption of benzene hexachlorides by the colloid was mainly physical adsorption and the stability of silicon dioxide sol was greater than that of ferric hydroxide after it adsorbed benzene hexachlorides.

Keywords: SiO₂ sol, Fe(OH)₃ colloid, Benzene hexachloride, Groundwater, Adsorption mechanism.

INTRODUCTION

Benzene hexachlorides (BHCs), also known as hexachlorocyclohexane, which possesses hydrophobicity and lipotropy, were once widely used due to their wide popularity, higher efficiency and lower cost, *etc.* Benzene hexachlorides possess high chemical, physical and biological stabilities, but it is extremely difficult for them to be decomposed in nature. Benzene hexachlorides were a sort of persistent organic pollutant (POPs). Water environment is one of the main places where benzene hexachlorides are gathered. Benzene hexachlorides were detected in the groundwater, pore water and surface sediments in the estuary of Minjiang in Fujian, China¹, the surface water of Qiantang river basin² and the surface water in Hangzhou³. Benzene hexachlorides were also detected in the Elbe river in Czech Republic⁴, Bahlui river in Romania⁵ and Ghaggar river in India⁶. Benzene hexachlorides in water bodies were extremely harmful to human's health, therefore, researches on the migration and transformation of benzene hexachlorides in water and earth media and their fate become a hot research area.

As an important component in the groundwater system, colloid is proved possessing exchange adsorption on the surface with metal ions, complex ions, some of the anions and

organic substances, *etc.*, forming binary and ternary surface complexes⁷, due to their structures and surface properties. Thus, colloids play an important role in adjusting the structure and function of the ecological system in the groundwater and they can adsorb pollutants in the groundwater effectively and significantly affect the migration of pollutants with low solubility in the groundwater⁸. Graham *et al.*⁹ studied the adsorption of pollutants by colloidal compounds in the pore water of soil with depleted uranium and the results revealed that both large (100 kDa-0.2 μm) and small (3-30 kDa) humic acid colloids are able to adsorb uranium. It was found by Ishikawa *et al.*¹⁰ that the adsorption of selenium by humic acid was accord with Freundlich's adsorption isotherm. It was discovered that, when combining with various pollutants, colloids would comply with the following basic reaction mechanisms: surface complexation, ion exchange and lyophobic partition *etc.*¹¹. However, in adsorption mechanism, it requires that the distance between the adsorbate and the adsorbent reached a certain order of magnitude¹² and charged property and surface property of the colloids were important factors directly affecting the adsorption of pollutants by colloids¹³. Adsorption of ammonium ion pollutants by colloids was researched and the result showed that higher ζ potential of the colloid and more chances to contact

ammonium ions would result in easier adsorption of ammonium ions and high stability of colloids¹⁴. Due to the aforementioned properties of colloids, it has been paid close attention about its influence on the pollutants in the groundwater. It was suggested that, after entering into the water environment, most benzene hexachlorides would be adsorbed by the suspended particles in the water bodies¹⁵, in which $\text{Fe}(\text{OH})_3$ colloid is the main component¹⁶. It was proposed by Nishioka that most of the "dissolved" (less than $0.45 \mu\text{m}$) Fe was colloidal¹⁷. As important components in the natural groundwater system, $\text{Fe}(\text{OH})_3$ colloid and SiO_2 sol possessed large specific area and could both adsorb various pollutants effectively. However, due to the different ζ potentials on $\text{Fe}(\text{OH})_3$ colloid and SiO_2 sol, their influences on the adsorption mechanism of benzene hexachlorides and the different adsorption mechanisms possessed by different zeta potentials required further investigation. In this paper, groundwater environment was simulated to study the adsorption behaviors of benzene hexachlorides by SiO_2 sol with negative zeta potential and $\text{Fe}(\text{OH})_3$ colloid with positive zeta potential. The colloid particle sizes and ultraviolet spectra of colloids before and after adsorbing benzene hexachlorides were investigated and the adsorption and distribution behaviors of benzene hexachlorides in the water by SiO_2 sol and $\text{Fe}(\text{OH})_3$ colloid were analyzed. It can provide scientific basis for further studies on the adsorption and migration of OCPs substances in shallow groundwater by colloids.

EXPERIMENTAL

GC-14C gas chromatograph and UV-2450 UV-visible spectra were purchased from Shimadzu Corporation (Japan); Zetasizer Nano ZS90 and Zeta Potential Analyzer were purchased from MALVERN Corporation (England); electron capture detector (ECD), fused silica capillary column DB-1 ($30 \text{ m} \times 0.32 \text{ mm} \times 0.25 \mu\text{m}$) and vacuum filter holder were also used in this study.

Benzene hexachlorides chromatographic standard sample was purchased from National Research Center for Certified Reference Material; cyclohexane, acetone and other agents used in the experiment were all analytical pure; acetone was used after redistillation. The water used in the experiment was reverse-osmosis ultrapure water.

Preparation of benzene hexachlorides standard solution: 2 mL of the purchased $50 \mu\text{g/mL}$ standard sample was dissolved in cyclohexane and diluted with cyclohexane to 50 mL in a volumetric flask to prepare $2 \mu\text{g/mL}$ standard stock solutions. Benzene hexachlorides standard solution was prepared and stored at 4°C for further use. The stock solution was diluted step by step to the concentration range of various components between 0.002 and $2 \mu\text{g/mL}$ using cyclohexane.

Preparation of benzene hexachlorides working solution: Weighted 10 g of 6% industrial benzene hexachloride powder and dissolved into 5 L ultrapure water, then stirred to better dissolved and filtered. After that, the concentration of the solution was determined and the solution was stocked for further use. The solution was further diluted to corresponding concentrations according to the requirements of the experiment.

Preparation of silicon dioxide sol: Weighted a certain amount of $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ and dissolved with water; then the

solution was cooled down in icy water and added hydrochloric acid solution with the concentration of 1:1 drop by drop while stirring to keep the pH value of the solution at about 2. Then the solution was stored at room temperature for 0.5 to 1 h for further use¹⁸.

Preparation of colloid ferric hydroxide: Weighted a certain amount of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and dissolved using water; then the solution was added into boiling ultrapure water drop by drop; after boiling for 5 min, refrigerated and diluted to volume.

Adsorption experiment: A certain amount of silicon dioxide sol and colloid ferric hydroxide were added into benzene hexachlorides solutions with various concentrations and then the mixture was diluted to volume, shaken up and kept standing. A certain amount of solution of each concentration was taken for determination of benzene hexachlorides in various phases according to separation determination procedures so to calculate benzene hexachlorides concentrations in various phases.

Separation steps: The obtained solution of each concentration was filtered using a vacuum filter holder and the filtrate was obtained after the solution passed through a $0.22 \mu\text{m}$ filter membrane. Then ultrafiltrate was obtained through a 1KD ultrafiltration membrane.

Extraction before analyzing and testing: Take a certain amount of filtrate and ultrafiltrate and put into a separatory funnel. Then 1 mL cyclohexane was added. After being adequately shaken for 3 min, the separatory funnel was stored for 3 min for stratification. The water phase was discarded. After the organic phase was dehydrated by using anhydrous sodium sulfate, it was ready for use in chromatographic analysis.

Determination by gas chromatography: Temperature programme: the initial temperature was 100°C . The temperature of the programme was increased by $10^\circ\text{C}/\text{min}$ till 220°C and then increased by $8^\circ\text{C}/\text{min}$ till 250°C ; then it was kept at this temperature for 10 min.

Analysis of colloid particle size: The sample bin of the Zetasizer Nano ZS90 and Zeta Potential Analyzer was opened and the sample cell was inserted into the sample pool to the bottom; and then the bin cover was closed. The sample was kept inside the instrument for approximately 5 min. After the sample reached preset temperature, the particle size was determined. The operation was conducted for 11 times.

Analysis by ultra violet spectrophotometer: Benzene hexachlorides, silicon dioxide sol, colloid ferric hydroxide, benzene hexachlorides + silicon dioxide sol and benzene hexachlorides + colloid ferric hydroxide were transferred into the 10 mm quartz colorimeter cell, respectively. With H_2O as the reference, spectrum scanning was performed on the samples between 190 nm and 400 nm in UV-2450 UV-visible spectrophotometer.

Calculation of determination results

Calculation of benzene hexachlorides concentration: Peak area external reference method was adopted to calculate the concentration of benzene hexachloride when chromatographic analysis was performed on benzene hexachloride.

Calculation methods for benzene hexachlorides in various phases: In the research, the total benzene hexachloride referred to the total benzene hexachloride content in the water

sample; colloid phase benzene hexachloride referred to the colloid benzene hexachloride content in the water sample that passed through the pre-filtration membrane with the pore size of 0.22 μm but retained by the ultrafiltration membrane with the molecular weight cut-off of 1KD (equal to 1 nm of pore size); true solution phase benzene hexachloride referred to the benzene hexachloride content in the ultrafiltrate after being filtered by 1KD ultrafiltration membrane. The relationship among these three items was as follows: total benzene hexachloride content = content of suspended solids phase benzene hexachloride + content of colloid phase benzene hexachloride + content of true solution phase benzene hexachloride. The suspended solids phase benzene hexachloride could be calculated according to the concentration of the total benzene hexachloride added into the system and concentrations of colloid phase benzene hexachloride and true solution phase benzene hexachloride.

RESULTS AND DISCUSSION

Influence of time on the distribution of benzene hexachlorides in various phases: According to the operation procedures, the prepared benzene hexachlorides (118.01 μg/L) + silicon dioxide sol (0.34 mg/L) and benzene hexachlorides (102.30 μg/L) + colloid ferric hydroxide (1.32 mg/L) solutions were sampled after 0, 0.5, 1, 2 and 5 days, respectively and the benzene hexachlorides in various phases were determined according to the separation steps. Figs. 1 and 2 displayed the distribution relationship of benzene hexachlorides with time in colloid phase, suspended solids phase and true solution phase in the water bodies of silicon dioxide sol, colloid ferric hydroxide, respectively.

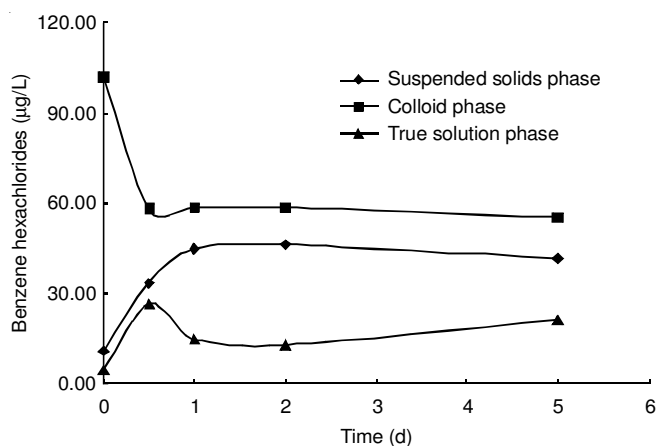


Fig. 1. Influence of time variation on the distribution of benzene hexachlorides with SiO₂ in various phases

As Fig. 1 shown, as soon as benzene hexachlorides solution was added into silicon dioxide sol, benzene hexachlorides transferred rapidly towards the silicon dioxide sol in the system. Among all the benzene hexachlorides, the proportion of distribution in colloid phase, in suspended solids phase and in true solution phase were 86.5, 9.33 % and 4.10 %, respectively. After 24 h, benzene hexachlorides in various phases basically reached equilibrium; the proportion turned out to be 49.7, 37.95 and 12.3 % correspondingly. After 5 days, there were 46.95 % of the benzene hexachlorides distributed in colloid

phase, 35.09 % distributed in suspended solids phase and 17.33 % distributed in true solution phase.

It was revealed in Fig. 2 that, when benzene hexachlorides solution had just been added into colloid ferric hydroxide, there were 48.97 % of the benzene hexachlorides distributed in colloid phase, 33.63 % in suspended solids phase and 17.40 % in true solution phase. With the prolongation of time, benzene hexachlorides concentrations in colloid phase increased slowly and the concentration of benzene hexachlorides in true solution phase decreased slowly, while the concentration of benzene hexachlorides in suspended solids phase increased first and then decreased. After 5 days, benzene hexachlorides in various phases basically reached equilibrium and the distribution ratio were 55.62, 16.53 and 27.80 % correspondingly in colloid phase, in suspended solids phase and in true solution phase.

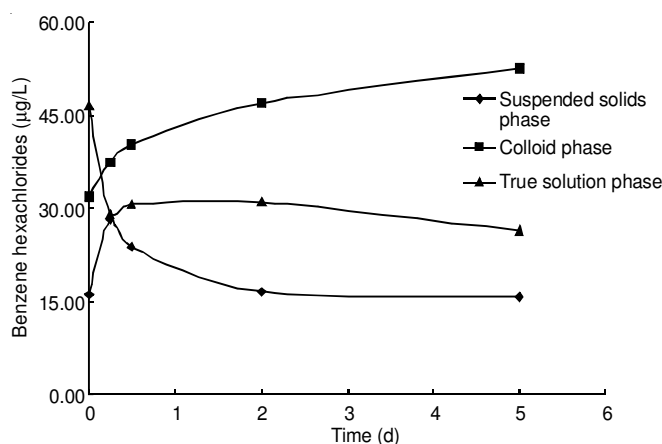


Fig. 2. Influence of time variations on the distribution of benzene hexachlorides with Fe(OH)₃ in various phases

It could be found by comparison that benzene hexachlorides could be adsorbed rapidly by silicon dioxide sol and adsorption equilibrium could be reached after 24 h. However, the adsorption of benzene hexachlorides by colloid ferric hydroxide was relatively slow and the adsorption amount of benzene hexachlorides in colloid phase kept increasing slowly all the time during the five observation days. After adsorption equilibrium phase was reached among various phases, the order of distribution coefficients for benzene hexachlorides with silicon dioxide sol in true solution phase, colloid phase and suspended solids phase in the system from low to high was as follows: $BHC_{\text{colloid phase}} > BHC_{\text{suspended solids phase}} > BHC_{\text{true solution phase}}$, the order of distribution coefficients for benzene hexachlorides in colloid ferric hydroxide system from low to high was as follows: while the distribution relationship in system, was as follows: $BHC_{\text{colloid phase}} > BHC_{\text{true solution phase}} > BHC_{\text{suspended solids phase}}$.

Influence of silicon dioxide sol and colloid ferric hydroxide on the UV spectrum of benzene hexachlorides: The UV spectral characteristics of BHCs and BHCs + colloid solution were shown in Figs. 3 and 4.

It could be seen from Figs. 3 and 4 that, in the UV zone (190 to 390 nm), the absorption of benzene hexachlorides reached peak at 203 nm; absorptions of silicon dioxide sol and colloid ferric hydroxide have no peak in the UV zone and silicon dioxide sol basically showed no absorption background

between 200 nm and 390 nm, while colloid ferric hydroxide showed strong absorption band (background) in the ultraviolet zone compared to that of silicon dioxide sol. The addition of the two colloids allowed the absorption peak of benzene hexachlorides solution at 203 nm to be remained. Moreover, ferric hydroxide can enhance the absorption peak of benzene hexachlorides, while silicon dioxide sol hardly affected the absorption peak of benzene hexachlorides. Thus it could be speculated that the adsorption of benzene hexachlorides by both silicon dioxide sol and colloid ferric hydroxide were physical adsorption.

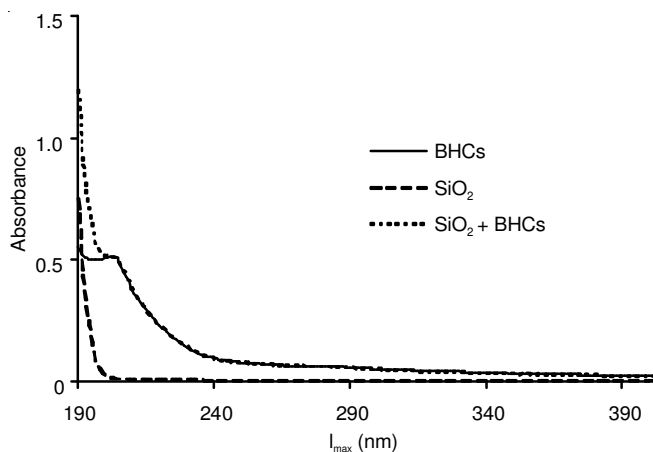


Fig. 3. Influence of silicon dioxide sol on the UV spectrum of benzene hexachlorides

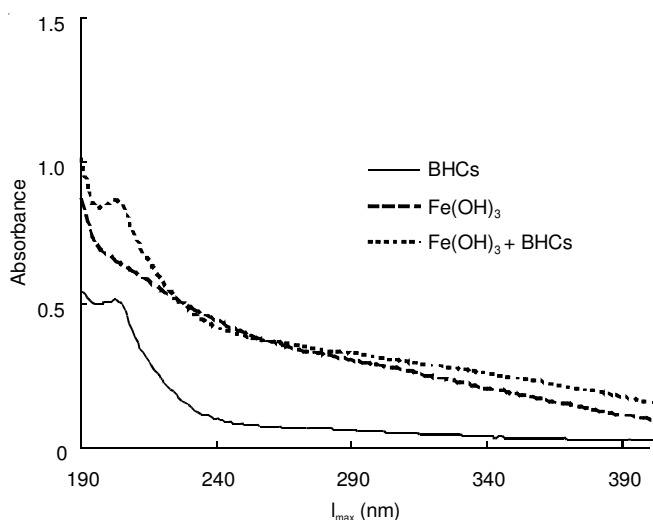


Fig. 4. Influence of colloid ferric hydroxide on the UV spectrum of benzene hexachlorides

Influence of the particle size characteristics of silicon dioxide sol and colloid ferric hydroxide on the distribution of benzene hexachlorides: Zetasizer Nano ZS90 and zeta potential analyzer were employed to determine the particle size characteristics of silicon dioxide sol, colloid ferric hydroxide, silicon dioxide sol and mixture of colloid ferric hydroxide + benzene hexachlorides and the results were shown in Figs. 5 and 6.

As demonstrated in Fig. 5, the particle size intensity distribution function of both silicon dioxide sol and benzene hexachlorides + silicon dioxide sol solution showed gradual increase with the growth of particle sizes and their distribution

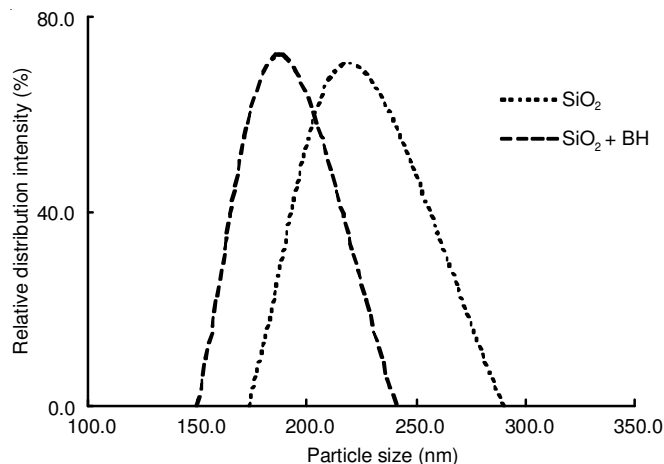


Fig. 5. Particle size distribution curve of SiO_2 and SiO_2 + benzene hexachlorides

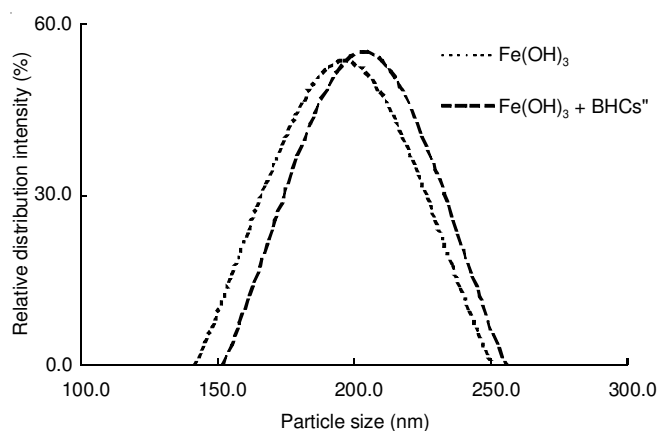


Fig. 6. Particle size distribution curve of $\text{Fe}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$ + benzene hexachlorides

function values reached the maximum at 218.94 nm and 187.53 nm, respectively; then the values reduced with the decrease of particle sizes, which was consistent with lognormal distribution. The particle size distribution range of silicon dioxide sol was between 174.12 nm and 289.92 nm with the distribution width of 115.80 nm and relative maximum distribution intensity of 70.40 %; the particle size distribution range of silicon dioxide sol + benzene hexachlorides was between 149.58 and 240.73 nm with the distribution width of 91.15 nm and relative max distribution intensity of 71.94 %. The addition of benzene hexachlorides resulted in the particle size of silicon dioxide sol + benzene hexachlorides becoming smaller.

According to Fig. 6, the particle size intensity distribution function of both colloid ferric hydroxide and benzene hexachlorides + colloid ferric hydroxide solution showed gradual increase with the growth of particle sizes and their distribution function value reached the maximum at 1195.96 and 203.51 nm, respectively. The values reduced with the decrease of particle sizes, which was consistent with lognormal distribution. The particle size distribution range of colloid ferric hydroxide was located between 141.8 and 250.12 nm with the distribution width of 108.32 nm and relative maximum distribution intensity of 53.5 %; the particle size distribution range of colloid ferric hydroxide + benzene hexachlorides was located between 151.69 and 255.32 nm with the distribution

TABLE-1
FITTING RESULTS OF ISOTHERMAL ADSORPTION CURVES OF BENZENE HEXACHLORIDES BY COLLOIDS

Fitting equation	Colloid	Model parameters	R ²
Henry equation	SiO ₂	K _d = 2.4496	0.9898
	Fe(OH) ₃	K _d = 1.5665	0.9965
Temkin equation	SiO ₂	a = -563.12 b = 207.88	0.9642
	Fe(OH) ₃	a = -18.131 b = 21.808	0.8997
Freundlic equation	SiO ₂	K _f = 0.6157 n = 1.2835	0.7718
	Fe(OH) ₃	K _f = 3.1156 n = 0.8348	0.9868
Langmuir equation	SiO ₂	Q _m = -3.4722 K _L = -0.1295	0.4664
	Fe(OH) ₃	Q _m = 344.8275 K _L = 0.00735	0.9676

width of 103.63 nm and relative max distribution intensity of 55.10 %. The addition of benzene hexachlorides resulted in the particle size of colloid ferric hydroxide + benzene hexachlorides becoming larger.

The comparison indicated that, the stability of colloid ferric hydroxide after adsorbing benzene hexachlorides was worse than that of silicon dioxide after adsorbing benzene hexachlorides and the former would form suspended substance easily; the particle size of benzene hexachlorides + colloid ferric hydroxide increased while that of benzene hexachlorides + silicon dioxide decreased.

Adsorption modes of benzene hexachlorides by silicon dioxide sol and colloid ferric hydroxide: Under experimental conditions, benzene hexachlorides of various concentrations were added into a certain amount of silicon dioxide sol and colloid ferric hydroxide, respectively. Then they were diluted to constant volume and were shaken up to allow them to be fully adsorbed by colloids. After adsorption equilibrium was reached, the solution was sampled; benzene hexachlorides in various phases were determined according to the separation steps and determination procedures and then the concentrations of benzene hexachlorides in colloid phase were calculated.

Isothermal adsorption curves of benzene hexachlorides by silicon dioxide sol and colloid ferric hydroxide was fitted by using Henry, Temkin, Freundlich and Langmuir equations, respectively. The results were shown in Table-1.

It was clear from Table-1 that the Henry's adsorption isotherm fitted the experiment results best, showing fairly good linear correlation. Its linear isothermal equation was as follows:

$$\text{Silicon dioxide sol: } C_{S1} = 2.4496 \cdot C_e1 + 5.654 \quad (R_1^2 = 0.9898)$$

$$\text{Colloid ferric hydroxide: } C_{S2} = 1.5665 \cdot C_e2 + 4.1912 \quad (R_2^2 = 0.9965)$$

where C_s (µg/L) was adsorption amount of benzene hexachlorides in colloid phase, C_e (µg/L) was concentration of benzene hexachlorides in liquid equilibrium phase.

It could be known from Table-1 that the adsorptions of benzene hexachlorides by both silicon dioxide sol and colloid ferric hydroxide were consistent with Henry's isothermal adsorption mode with fairly good linear dependence. It could also be seen from the distribution coefficients that the adsorption ability of benzene hexachlorides by silicon dioxide sol was greater than that by colloid ferric hydroxide, which indicated that the benzene hexachlorides adsorption degree by SiO₂ sol with negative potential was greater than that by Fe(OH)₃ colloid with positive potential.

Conclusions

(1) As inorganic colloids, SiO₂ and Fe(OH)₃ had strong adsorption ability for benzene hexachlorides and the adsorption ability of silicon dioxide for benzene hexachlorides was greater than that of colloid ferric hydroxide. (2) After adsorbing benzene hexachlorides, the particle size intensity distribution functions of two kinds of colloids were in line with the lognormal distribution and the silicon dioxide with benzene hexachlorides was more stable than colloid ferric hydroxide. (3) Adsorptions of benzene hexachlorides by SiO₂ and Fe(OH)₃ were physical. (4) Adsorptions of SiO₂ and Fe(OH)₃ for benzene hexachlorides were consistent with Henry's isothermal adsorption mode. Both of them showed fairly good linear correlation.

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