



New evidence for the importance of Mn oxides contributed to nitrobenzene adsorption onto the surficial sediments in Songhua River, China

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ABSTRACT

Nitrobenzene at a relatively high concentration was reported to cause an environmental pollution event in Songhua River, China in 2005. The adsorption characteristics of nitrobenzene on the surficial sediments (natural surface coatings) were investigated via a selective extraction – adsorption – statistical analysis method. The experimental results show that the changes in the adsorption potential are not always consistent with the variation of particle structure, suggesting that the effect of removal of some components by extraction or separation procedures on the adsorption potential is much greater than that of variation of particle structure. An additional model analysis indicates that not only organic materials but also Fe oxides, Mn oxides and clay minerals contribute much to the adsorption of nitrobenzene. But the adsorption capacity of Mn oxides on a unit mass basis is the highest, and the lowest for clay minerals except for silicate minerals, implying that the role of organic materials and clay minerals in the solid particles contributed to binding of nitrobenzene is less than that of Fe and Mn oxides, especially the later. The new evidence for the higher adsorption potential of nitrobenzene on the surficial sediments (natural surface coatings) and the more importance of Mn oxides contributed to nitrobenzene adsorption is showed in the present study supposing that the adsorption capacity of solid particles can be divided into several fractions.

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1. Introduction

Nitroaromatic compounds have been widely used as intermediates in the preparation of dyes, perfume, fuels, drugs, explosives, pesticides, and other macromolecular organic chemicals [1–3]. Nitrobenzene, one of monocyclic nitroaromatic compounds and listed as priority toxic pollutants by USEPA, is an important raw material and product of the chemical industry [3,4], and a toxic synthetic chemical that targets multiple organs by all routes of exposure [4,5].

An explosion of petrochemical plant occurred in Jilin Province, China, on November 13, 2005, and approximate 100 tons of toxic substances including benzene, aniline and nitrobenzene were spilled into the Songhua River, China (SEPA). The nitrobenzene pollution of Songhua River has attracted more public concern on the fate of nitrobenzene in the river. After the spilling, nitrobenzene might enter the sediments and pose dangers to the aquatic organ-

isms and public health, although the concentration of nitrobenzene in the river decreased rapidly as the pollution plume moved downriver due to dilution, volatilization, deposition, etc (SEPA). To determine the environmental and public health effects, an emergency monitoring program was initiated; investigations on environmental behaviors and toxicity assessments of nitrobenzene in the Songhua River were also carried out. These studies mainly focused on the transformation of nitrobenzene, however, such as photolysis [5,6], biodegradation [7], and volatilization [5], but less on the adsorption of nitrobenzene.

Aqueous nitrobenzene in the river can be transferred to air and solid particles via diffusion and partition, and transformed to other species via photolysis, hydrolysis and biodegradation. All these processes may affect the behavior and fate of nitrobenzene in the aquatic environment. Among the different transference and transformation processes, adsorption of sediments is an important one influencing the fate of nitrobenzene in the Songhua River, although the environmental behavior of nitrobenzene predicted by EXAMS computer model shows that volatilization contributed most to nitrobenzene transference and transformation [8], and the nitrobenzene has exhibited a moderate adsorption potential and relative mobility in most kinds of soil and sediments as indicated by previous experimental results [9–11]. The concentration

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of nitrobenzene in the Songhua River after the pollution was much higher within several days, and even on November 25, 2005, about 12 days later the highest concentration of nitrobenzene in Songhua River was still up to 0.581 mg/L [5]. It is well known that nitrobenzene is 1.2 times as dense as water, and therefore has a potential to deposit at the bottom of river water where it can be bound by the sediments. The more nitrobenzene in the water leads to more nitrobenzene transferring to the bottom of river, and furthermore gives rise to more opportunity for reaction between nitrobenzene and sediments.

Surficial sediments in river play an important role in influencing the pollution of river water, and act as both carriers and potential sources of contaminants in an aquatic environment. Natural surface coatings, a unique insulating layer that must be reached and crossed before a contaminant contacts with the surficial sediments supporting the surface coatings [12], also play a critical role in determining the fate of contaminants in aquatic environment and can be considered as a special kind of surficial sediments [13–17]. These two kinds of solid particles consist of minerals, including Fe oxides, Mn oxides and clay minerals, and organic materials, which contain different domains that play different roles in the adsorption of organic contaminants [18]. Up to now, the studies on the roles of sediment components mainly focus on organic materials because most studies indicate that organic materials are identified as predominant sorbents unless the content of organic carbon is below 0.1% by mass [19,20]. However, other components except for organic materials may also indirectly contribute to the adsorption of organic pollutants although there is no its direct contribution, because the interactions between various sediment components generally take place. For instance, both organic matter and metal oxyhydroxides may coat surfaces of silicate minerals changing their affinity to organic pollutants [21]. Researches on the adsorption behaviors of nitrobenzene in the sediment components, including not only organic materials, but also iron oxides, manganese oxides, and clay minerals have been rarely reported.

The objective of the present study is to investigate the transport behavior of nitrobenzene in the water/sediment system. The selective extraction-adsorption-statistical analysis method is used to reveal how nitrobenzene is eliminated from the polluted water to surficial sediments (surface coatings). These results will be helpful for getting insight to the environmental behavior and risk assessment of nitrobenzene in Songhua River.

2. Materials and methods

2.1. Sorbents

Surficial sediments, approximately 5 cm in depth from the surface, were collected with a plastic scoop and stored in polyethylene bags. Shingles in the near bank of the river were taken out of the water, and natural surface coatings attaching to the shingles were scraped using a plastic scoop into plastic container. Then the particulate samples were transported to the laboratory and freeze-dried. The agglomerates in the sample were broken and grounded through a mortar. Particulates with diameter of larger than 0.25 mm were discharged by sieving. All further analyses were carried out on the particulates with diameters of less than 0.25 mm.

The pretreated surficial sediment was then split into six equal portions. Three portions of sediment were extracted with different chemical reagents including $\text{NH}_2\text{OH}\cdot\text{HCl}$, $(\text{NH}_4)_2\text{C}_2\text{O}_4$ and H_2O_2 in isolation to remove target components [22]. The other two portions of sediment were sequentially extracted with H_2O_2 (30%) and 0.2 M $(\text{NH}_4)_2\text{C}_2\text{O}_4$ in order to obtain the particulate samples after removal of organic materials and Fe/Mn hydrous oxides. Then one of the above obtained particulate samples was followed by further separation via suspending and re-precipitation to obtain the clay

minerals and silicate residues. The last one portion of sediment without any extraction procedure was only considered as the control to be compared with. All solid samples were washed six times with distilled water and freeze-dried.

2.2. Sorption experiment

Adsorption of nitrobenzene onto the various sediment samples was determined in duplicate using the batch equilibration method. For each determination, 0.5 g of freeze-dried sediment was mixed with 100 mL of initial solution containing 0.5, 1, 2, 4, 6, 8, 10, 15 mg/L of nitrobenzene, 200 mg/L of NaN_3 to minimize biological activity, and 1 mM $\text{CaCl}_2 + 0.1 \text{ mM MgCl}_2 + 0.5 \text{ mM Na}_2\text{B}_4\text{O}_7$ to simulate the on-site river condition and keep the background electrolyte and hardness similar to that of river water. Before added to the conical flasks, the pH values of the solutions were adjusted to 7.0 ± 0.5 using 0.01 M HCl or 0.01 M NaOH . The suspensions were stirred continuously h at room temperature (25°C) for 24 on a shaker in 250 mL conical flasks with glass stopples. The pH values of suspensions were kept as invariable as possible through readjusting to 7.0 ± 0.5 every 2 h in the initial stage of 24 h or 4 h in the later stage of 24 h. Following equilibration, the suspensions were centrifuged at 3800 rpm for 20 min and then passed through membrane filter with 0.22 μm pore size. The PCP concentration in the supernatant was determined to assess the nitrobenzene adsorption during the reaction between the nitrobenzene and sediments. It must be noted that only 0.05 g of clay minerals was used in the adsorption experiment since the yield of clay minerals separated from the sediments was about 10%. An experiment on reaction between nitrobenzene and natural surface coatings were also carried out as that applied to reaction between nitrobenzene and surficial sediments.

2.3. Analytical procedures

Reduction – Azo – photometry was employed to analyze nitrobenzene concentration. The detection limit of this method was 0.2 mg/L. A TOC-analyzer (TOC-V_{CPH}, Shimadzu, Japan) was used to determine total organic carbon in the solid particles, and digestion of $\text{HNO}_3\text{--HClO}_4$ followed by a flame atomic adsorption spectrometer (WYX-9004, Shenyang, China) analysis was applied to measure pseudo-total Fe and Mn in the solid particles. Total amounts of extractable Fe and Mn oxides in the particles were measured by using a modified sequential extraction procedure [23–25].

BET surface area of all the samples was determined on a surface area and pore size analyzer (TriStar 3000, Micromeritics, USA). An environmental scanning electron microscopy (PHILIPS XL-30, Philips-FEI, the Netherlands) was used to investigate the surface and structural characteristics of the solids. An X-ray diffraction diffractometer (XRD-6000, Shimadzu, Japan) with $\text{CuK}\alpha$ radiation at 40 kV and 30 mA was used. Solids used for XRD analysis were freeze-dried, crushed, and mounted on a glass sample holder. XRD patterns were collected using a step-scanning rate of $0.06^\circ 2\theta/\text{s}$ for all the samples except for the clay minerals, XRD patterns of which were collected at a step-scanning rate of $0.02^\circ 2\theta/\text{s}$.

2.4. Data analyses

The percentage of removal after extractions with $\text{NH}_2\text{OH}\cdot\text{HCl}$, $(\text{NH}_4)_2\text{C}_2\text{O}_4$, and H_2O_2 were calculated by using the formula: % Removal = $\frac{\text{pseudo-total content} - \text{particle content after extraction}}{\text{total extractable amount}} \times 100\%$

In the nitrobenzene adsorption experiment, the mass of nitrobenzene that was lost from solution of equilibrium was assumed to be absorbed by the solid particles, and nitrobenzene adsorption was described using the Langmuir isotherm, which works well for heterogeneous adsorbents. The adsorption

Table 1
Contents of metal oxides and organic materials in the solid particles pretreated by different procedures including sequential and selective extractions.

Samples	Pretreatments	Fe		Mn		Organic materials	
		Content ($\mu\text{mol Fe/g}$)	Removal (%)	Content ($\mu\text{mol Mn/g}$)	Removal (%)	Content ($\mu\text{mol C/g}$)	Removal (%)
Surficial sediments	HNO ₃ -HClO ₄	491.79 \pm 0.36		12.32 \pm 0.30		1849.92 \pm 17.69	
	MSEP	304.43 \pm 4.49	100	2.56 \pm 0.01	100	251.44 \pm 6.33	100
	NH ₂ OH·HCl	464.48 \pm 4.71	14.40	4.61 \pm 0.06	78.94	1685.82 \pm 21.23	10.27
	(NH ₄) ₂ C ₂ O ₄	332.25 \pm 1.71	85.15	4.49 \pm 0.04	80.19	1760.24 \pm 23.34	5.61
	H ₂ O ₂	482.84 \pm 1.89	4.78	10.53 \pm 0.13	18.28	367.16 \pm 10.25	92.76
Surface coatings	HNO ₃ -HClO ₄	513.22 \pm 6.92		13.63 \pm 0.06		4589.59 \pm 18.19	
	MSEP	309.15 \pm 2.71	100	2.77 \pm 0.07	100	297.66 \pm 7.91	100
	NH ₂ OH·HCl	486.42 \pm 7.59	13.13	4.07 \pm 0.25	88.11	4178.54 \pm 34.93	9.58
	(NH ₄) ₂ C ₂ O ₄	339.41 \pm 1.76	85.17	4.41 \pm 0.04	84.89	4434.15 \pm 26.26	3.62
	H ₂ O ₂	502.95 \pm 6.36	5.03	11.76 \pm 0.83	17.19	660.06 \pm 12.37	91.56

Average ($n=3$) \pm a standard deviation.

parameters of Langmuir isotherm were determined by non-linear regression based on the equilibrium results.

3. Results

3.1. Characterization of solid particles

The composition of the original surficial sediments (surface coatings) indicates that these two solid particles have the same tendency of contents of Fe oxides > Mn oxides and the ratio of Fe/Mn are about 40 (Table 1). The contents of both Fe and Mn oxides in the surface coatings are greater than those in surficial sediments but no significant deviation (<10%) is observed. Total amount of extractable Fe oxides in the surficial sediments (surface coatings) is only 40% of pseudo-total Fe oxides, and the percentage of total amount of extractable Mn oxides is increased nearly up to 80% of the pseudo-total Mn oxides. The content of organic materials in the surface coatings is approximately 2.5 orders of magnitude higher than that in the surficial sediments. This obviously higher content of organic materials is important for reaction between organic pollutant and surface coatings as mentioned in the former studies [26,27].

After extraction, the NH₂OH·HCl reagent removed 78% and even more of Mn oxides from the non-residual fraction of the solid particles, and only less than 9% of organic materials and 15% of Fe oxides were also extracted. More than 80% of Fe and Mn oxides were removed from the non-residual fraction of the particles and only 5% of organic materials were extracted simultaneously after extraction with (NH₄)₂C₂O₄-H₂C₂O₄ solution. After extraction with H₂O₂, 80% of organic materials could be removed from the solid phases with less effect on Fe oxides (5%). However, about 18% of Mn oxides were also extracted which can be explained by the binding form of Mn oxides in the surficial sediments (surface coatings) [22].

It can be found in Table 2 that the surface area of surface coatings is greater than that of surficial sediments whether the solid phases are treated with reagents or not. Meanwhile, it can also be found that the surface area of surficial sediments (surface coatings) significantly changes after each extraction, and all increase compared to the untreated solid particles except for that of silicate residues.

Table 2
BET surface area of the solid particles pretreated by different procedures (m²/g).

Pretreatments	Surficial sediments	Surface coatings
Sediments untreated	16.78	24.27
Sediments treated with NH ₂ OH·HCl	20.80	27.08
Sediments treated with (NH ₄) ₂ C ₂ O ₄	19.65	28.42
Sediments treated with H ₂ O ₂	29.87	43.20
Sediments treated with H ₂ O ₂ and (NH ₄) ₂ C ₂ O ₄	28.98	44.12
Clay minerals	91.24	100.04
Silicate residues	13.94	20.11

The scanning electron micrograph, X-ray powder diffraction pattern and infrared spectroscopy of the solid particles indicate that the treatments with NH₂OH·HCl and (NH₄)₂C₂O₄-H₂C₂O₄ affect less on the structural characteristics of particulates and thus are not presented in the present study. After H₂O₂ extraction, the dispersion degree of the solid particles enhances, as well as more distinct of the crystal structure can be found (Fig. 1). The SEM micrographs of H₂O₂-treated solid particles reveal many small particles between and apparently coating the surface of large particles, but not completely for the presence of some relatively smaller mineral particles. In Fig. 2 it can be found that these small mineral particles are clay minerals, which are dominated by laminar and layered particles with diameter less than 5 μm based on the morphological measurement. The removal of Fe/Mn oxides and organic materials make the surfaces of clay minerals and silicate residues clean (Fig. 2C and D), and the clay minerals (or silicate residues) are coated with Fe/Mn oxides (or organic materials), implying existence of some interactions between the clay minerals (or silicate residues) and Fe/Mn oxides (or organic materials).

XRD patterns of the clay minerals in the surficial sediments (surface coatings) are presented in Fig. 3. The clay minerals in the surficial sediments (surface coatings) consist of illite, kaolinite, chlorite, and illite/montmorillonite mixed layer corresponding to 50.7%, 13.9%, 14.2% and 21.2% (57.1%, 16.1%, 15.6% and 11.2%) of the total clay minerals, respectively. Meanwhile, the XRD patterns of untreated solid particles indicate that the non-clay minerals are dominated by quartz and orthoclase (not present here).

FTIR spectra of untreated and H₂O₂-treated surficial sediments (surface coatings) are shown in Fig. 4. Also shown in Fig. 4 are the differential FTIR spectra. Two major absorbance bands of 3700–2700 and 1700–900 cm⁻¹ are clearly evident in these differential FTIR spectra. Organic functional groups likely contributed to the absorbance band of 3400–3000 cm⁻¹ are -COOH and -OH, and C-H stretching is attributed to the absorbance band of 3000–2800 cm⁻¹.

3.2. Adsorption of solid particles

Adsorption of nitrobenzene described by Langmuir isotherm is shown in Fig. 5. The results show that the adsorption behaviors of nitrobenzene on the untreated solid particles and silicate residues can be adequately described by Langmuir isotherm with $R \geq 0.90$, and the adsorption thermodynamics of nitrobenzene on the other solid particles with different treatments are similar to those and not be presented here. Although the adsorption of organic pollutants on soil or sediment is generally well fitted with a linear model as reported [9,28–31], the adsorption of nitrobenzene onto the silicate residues (Fig. 5) as well as on the solid particles treated with H₂O₂ as investigated in the present study is not fitted well with the linear model. So, all the adsorption data were analyzed with Lang-

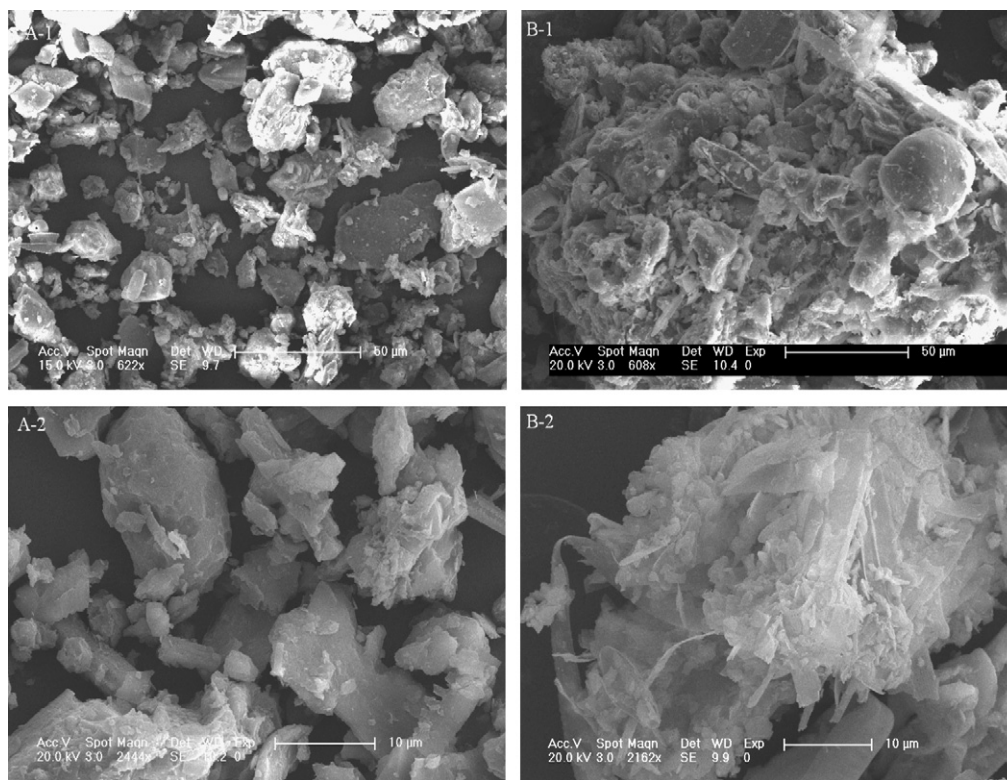


Fig. 1. Scanning electron micrographs of the original surficial sediments (A-1) and surface coatings (B-1); and surficial sediments (A-2) and surface coatings (B-2) after H₂O₂ extraction.

muir isotherm in order to distinguish the variation between the untreated particles and particles after different treatments.

The Γ_{\max} , which to a certain extent represents an affinity between pollutants and the sediment or soil, is listed in Table 3.

Generally the adsorption capacity of surface coatings is greater than that of surficial sediments, and all the treatments on the solid particles affect the adsorption behaviors of the solid particles. The amount of adsorbed nitrobenzene decreases by 23% and 27% for

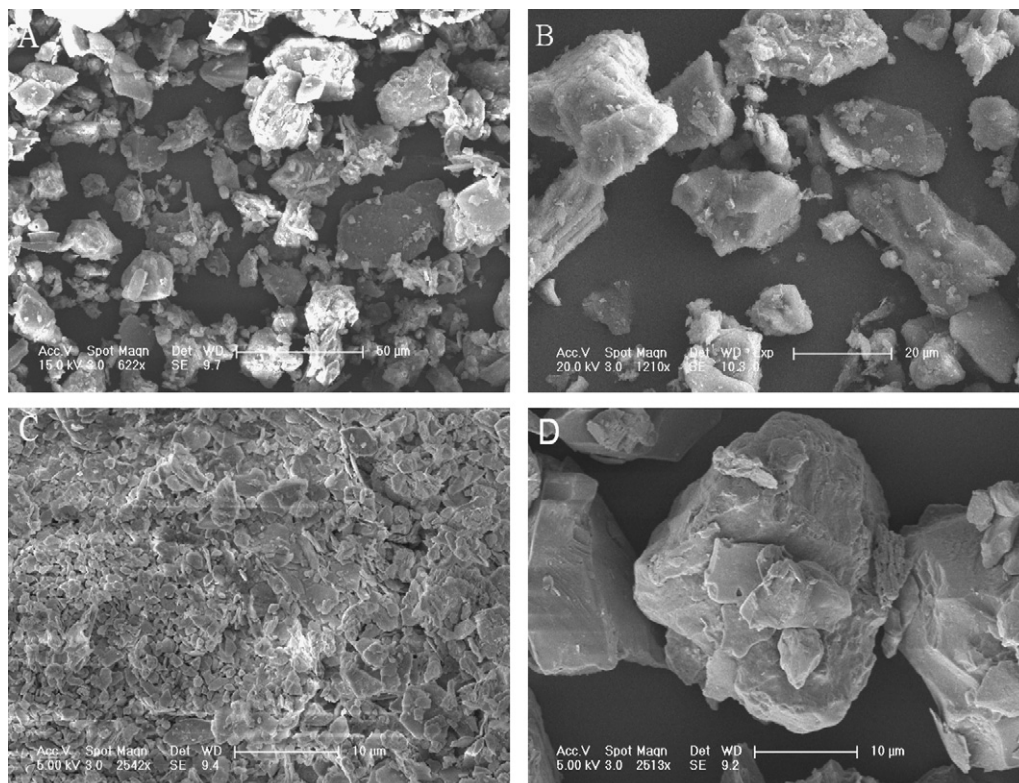


Fig. 2. Scanning electron micrograph of the surficial sediments (A), residues (B), clay minerals (C) and silicate residues (D).

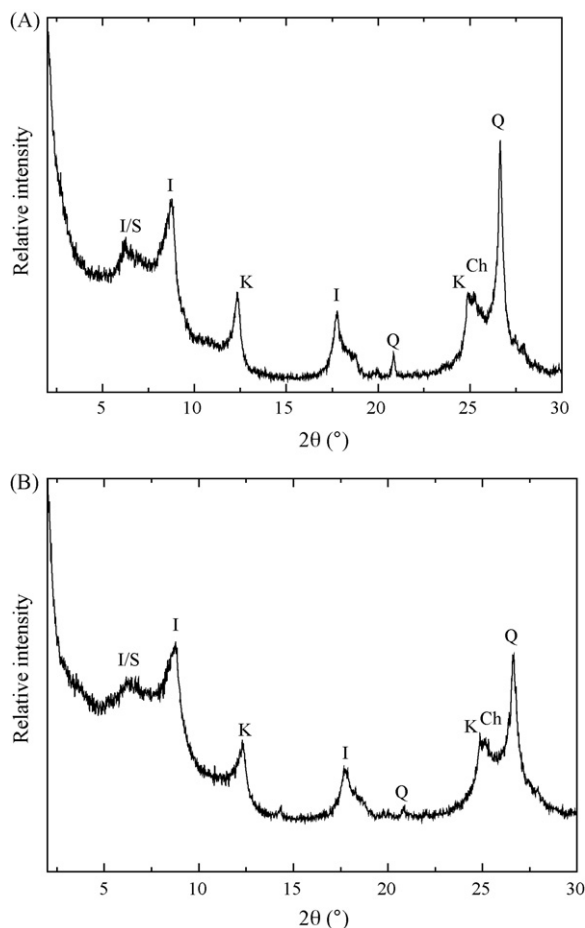


Fig. 3. X-ray diffraction spectra of the clay mineral separated from surficial sediments (A) and surface coatings (B) saturated by glycol.

the surficial sediments and the surface coatings after removal of Mn oxides, and also a similar tendency is obtained for the solid particles after treated with $(\text{NH}_4)_2\text{C}_2\text{O}_4$ or H_2O_2 (Table 3). When organic materials and Fe/Mn oxides are all removed from the solid particles, the binding ability of the solid particles reaches a lower value. These results imply that organic materials and Fe/Mn oxides in the solid particles facilitate the adsorption of nitrobenzene. Also the adsorption of nitrobenzene on the silicate residues after separation of clay minerals decreases, and the amount of adsorbed nitrobenzene is only corresponding to 1/3 of that of the untreated solid particles. But the adsorption capacity of clay minerals is significantly increased with approximately two orders of magnitude greater than that of the untreated solid particles.

Compared with the nitrobenzene adsorption on surficial sediments in a previous study [11], it can be found that the adsorption values shown in Table 3 in the present study are much higher. This fact can be explained by the difference in experiment conditions applied in these two studies. The sediment particles used in the present study were broken and grounded through a mortar, and the particulates with diameter of larger than 0.25 mm were discharged by sieving. But in the reported study the sediments used were mainly comprised of silt (0.05–0.002 mm) and sand (2.0–0.05 mm), and the particle size of partial particles in the reported study was larger than that of the present study. This difference induced the higher nitrobenzene adsorption due to the smaller particles in the present study. The nitrobenzene adsorption experiments were conducted at $0.8 \pm 0.2^\circ\text{C}$ in the reported study and the temperature ($25 \pm 1^\circ\text{C}$) in the present study was much higher. The temperature

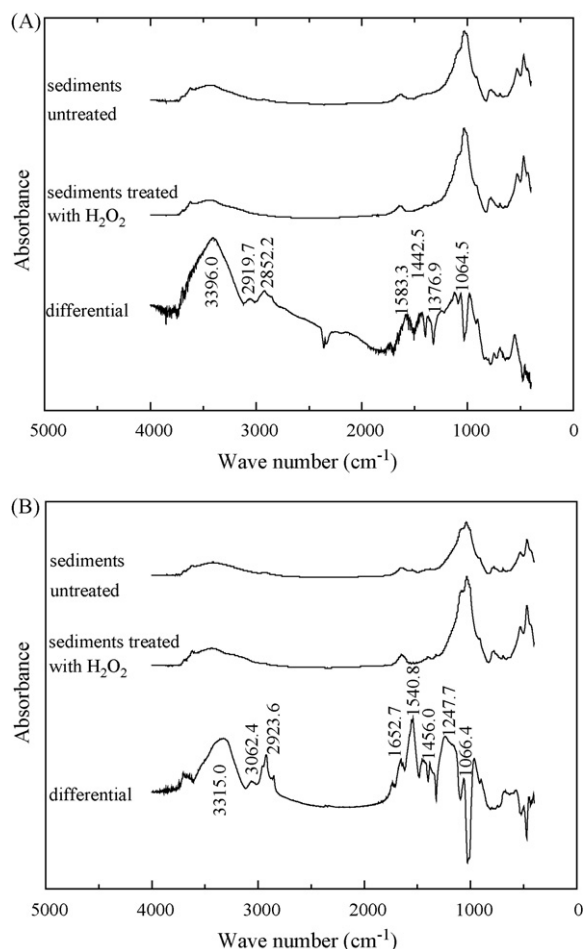


Fig. 4. Differential infrared spectra of surficial sediments (A) and surface coatings (B) obtained by spectra subtraction.

change may lead to higher adsorption capacity of nitrobenzene in the present study than that in the reported study.

4. Discussion

4.1. Relationship between adsorption capacity and structure and component of particulate

The results of extraction and adsorption experiments indicate that the treatments with $\text{NH}_2\text{OH}\cdot\text{HCl}$, $(\text{NH}_4)_2\text{C}_2\text{O}_4\text{--H}_2\text{C}_2\text{O}_4$, and H_2O_2 indeed affect structure and adsorption characteristics of the solid particles, and the changes in adsorption behavior were not always consistent with the variation of structure of the solid particles, which is more or less varied after treatment with $\text{NH}_2\text{OH}\cdot\text{HCl}$, $(\text{NH}_4)_2\text{C}_2\text{O}_4\text{--H}_2\text{C}_2\text{O}_4$ and H_2O_2 as proved by SEM, XRD and FTIR results. The surface of particles was much cleaner after treated with H_2O_2 , and was clean to a less degree after treated with $\text{NH}_2\text{OH}\cdot\text{HCl}$ and $(\text{NH}_4)_2\text{C}_2\text{O}_4\text{--H}_2\text{C}_2\text{O}_4$. This variation of surface structure may partly contribute to the decrease of adsorption capacity of solid particles. However, the surface area of these treated particles obviously increased compared with the original particles, which would be in favor of adsorbing nitrobenzene; however the experimental results were just opposite. Although the surface area was increased, the amount of adsorbed nitrobenzene on these particles was decreased.

The components of solid particles treated with $\text{NH}_2\text{OH}\cdot\text{HCl}$, $(\text{NH}_4)_2\text{C}_2\text{O}_4\text{--H}_2\text{C}_2\text{O}_4$ and H_2O_2 was significantly varied as proved by the extraction efficiency analysis. Extraction with the above reagents induced the removal of Mn oxides, Fe oxides or organic

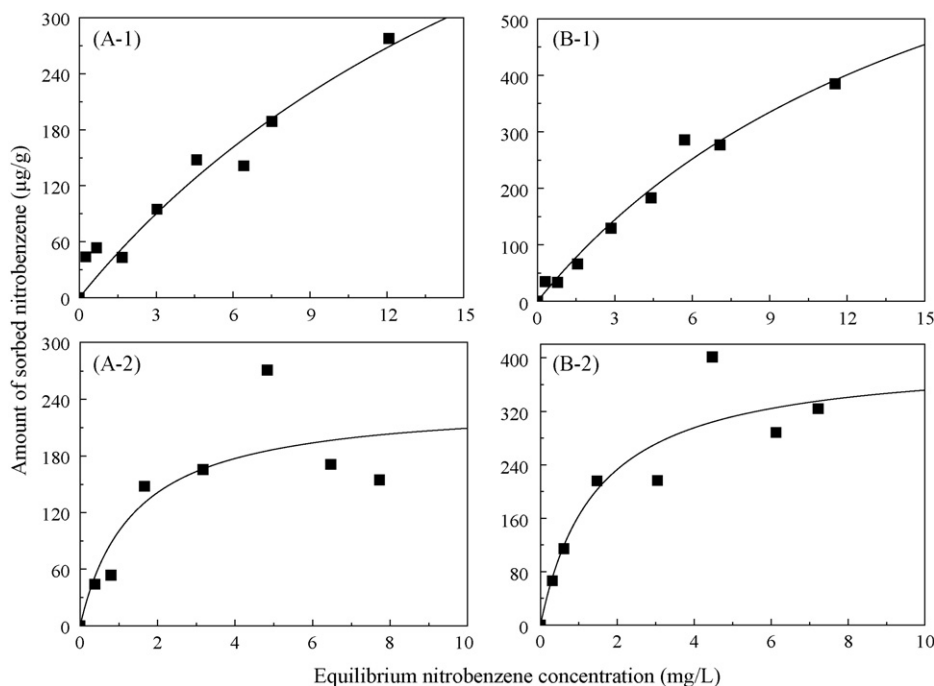


Fig. 5. Langmuir isotherms of nitrobenzene adsorbed on the original surficial sediments (A-1) and surface coatings (B-1); and silicate residues separated from surficial sediments (A-2) and surface coatings (B-2).

materials, and as a result, the adsorption capacity of particles was decreased with the removal of these components. The more components removed, the more adsorption capacity decreased. For example, the adsorption capacity of the particles after treated with $(\text{NH}_4)_2\text{C}_2\text{O}_4\text{-H}_2\text{C}_2\text{O}_4$ to remove most Fe and Mn oxides was much lower than that of the particles after treated with $\text{NH}_2\text{OH}\cdot\text{HCl}$ to remove most Mn oxides only, and that of the particles, which was sequentially treated with H_2O_2 after treated with $(\text{NH}_4)_2\text{C}_2\text{O}_4\text{-H}_2\text{C}_2\text{O}_4$ to further remove organic materials was lowest among these three particles. These results suggest that the contribution of surface area to the increase of adsorption capacity was negligible compared with the decrease of adsorption capacity caused by removal of Fe oxides, Mn oxides or organic materials removal, because the decrease in adsorption due to the removal of Fe oxides, Mn oxides and organic materials was more significant than the increase in adsorption due to the increase of BET surface area after the solid particles treated with $\text{NH}_2\text{OH}\cdot\text{HCl}$, $(\text{NH}_4)_2\text{C}_2\text{O}_4\text{-H}_2\text{C}_2\text{O}_4$ and H_2O_2 . Therefore, it is important to understand the contribution of the above components to the adsorption capacity of solid particles without considering the effect of the structural variation.

The adsorption capacity of clay minerals separated from the solid particles was much greater than that of any other particles. The BET surface area of clay minerals is about five orders of magnitude

larger than that of original solid particles (Table 2). The previous studies indicated that the surface areas of solid particles have been proved to play a role in adsorption (a surface phenomenon), and generally the larger the surface area, the higher the adsorption capacity [32,33]. Also an important factor influencing the adsorption capacity of solid phase is the surface charge of solid phase, and the greater surface charge of the solid phase, the greater affinity capacity of solid phase [33,34]; the illite/montmorillonite mixed layer is an expandable clay mineral, and the surface charge of these clay minerals is relatively larger than that of the solid particles (Fig. 3).

As the composition of solid particles especially the contents of Fe oxides, Mn oxides, organic materials and clay minerals was an important factor influencing the adsorption capacity of solid particles, the adsorption capacity of surface coatings was much greater than that of surficial sediments. The content of clay minerals in the surficial sediments is of 132.2 mg/g, however, the surface coatings have a much higher clay content of 152.1 mg/g, not to mention the contents of Fe oxides, Mn oxides and organic materials. Meanwhile, the surface area of surface coatings is much greater than that of surficial sediments (Table 2), the dispersion degree of the surface coatings is also much greater than that of the surficial sediments (Fig. 1), and the same results are obtained for the relative absorbance intensity of organic functional groups including $-\text{COOH}$

Table 3
Nitrobenzene adsorption potential on the solid particles pretreated by different procedures evaluated by Langmuir isotherm.

Pretreatments	Surficial sediments		Surface coatings	
	Adsorption potential ($\mu\text{g/g}$)	Adsorption potential variation (%)	Adsorption potential ($\mu\text{g/g}$)	Adsorption potential variation (%)
Particles untreated	786.03 ± 44.75	Control	982.02 ± 27.63	Control
Particles treated with $\text{NH}_2\text{OH}\cdot\text{HCl}$	603.59 ± 23.96	-23.21	714.86 ± 9.45	-27.21
Particles treated with $(\text{NH}_4)_2\text{C}_2\text{O}_4$	424.01 ± 13.65	-46.06	576.39 ± 17.12	-41.31
Particles treated with H_2O_2	430.93 ± 20.31	-45.18	465.33 ± 9.22	-52.62
Particles treated with H_2O_2 and $(\text{NH}_4)_2\text{C}_2\text{O}_4$	323.26 ± 20.69	-58.87	403.24 ± 17.15	-58.94
Clay minerals	1930.40 ± 78.98	145.59	2037.36 ± 114.53	107.47
Silicate residues	238.35 ± 15.91	-69.68	365.24 ± 17.57	-62.81

Average ($n = 2$) \pm an average deviation.

and –OH. These differences in structural characteristics may also result in a difference between adsorption capacities of surficial sediments and surface coatings.

4.2. Relative contribution and adsorption capacity of components

The adsorption capacities of the clay minerals and silicate residues in the solid particles can be more easily determined as these two components can be easily separated from the solid particles as shown in Table 2. However, the other components such as organic materials, Fe oxides and Mn oxides are impossible to be obtained through the separation method, and not to mention determining the adsorption abilities of these components via directly adsorption experiment. As none of extraction techniques removes only one component without any effect on other components, thus accurate determination of the adsorbed nitrobenzene by each individual component requires consideration of contributions of the other components [16,17]. In the present study, the nitrobenzene adsorption data are analyzed using nonlinear least-squares fitting (NLSF) by MicrocalOrigin (Version 6.0, Microcal Software, Inc. Northampton, MA) to estimate the adsorption parameters of each component. The model used for the analysis considered total adsorption by unextracted and extracted solids at a given nitrobenzene concentration (Γ_{total}) to be the sum of contributions from the four constituents (Fe and Mn oxides, TOC, and Residues) as expressed by the Langmuir adsorption isotherm [16,17]:

$$\Gamma_{\text{total}} = \sum_{i=1}^4 C_i \frac{\Gamma_i^{\text{max}} K_i [\text{NB}]}{1 + K_i [\text{NB}]} \quad (1)$$

where, for each component, C_i is the total concentration of the extractable component (mg metal or TOC g^{-1}) in the solids, and the fraction term represents its adsorption ability (mg per g metal or per g TOC). In the fraction term, Γ_i^{max} is the maximum of the adsorbed nitrobenzene by component i , and K_i is the Langmuir equilibrium constant.

The adsorption data of nitrobenzene on unextracted and extracted solid particles were fitted using multiple data sets fitting. Before fitting, Γ_i^{max} and K_i were set as shared parameters and were initialized based on the assumption that each component had the same adsorption ability. Then iterations were performed until X^2 was not reduced (the fitting converged) or X^2 did not change in three iterations (the fitting did not converge), where X^2 was used to represent the deviations of the theoretical curves from the experimental data.

The relative contribution of different components calculated by an additional model indicates that organic materials, Fe oxides, Mn oxides and residues in the solid particles facilitate the adsorption of nitrobenzene (Table 4). This agrees well with the results of differential infrared spectra as shown in Fig. 4. Organic functional groups such as –COOH and –OH have been proved to exist in the organic fraction of solid particles and these functional groups would contribute most to adsorption of nitrobenzene on the solid particles. On the other hand, the previous studies proved that

organic pollutants could be adsorbed on solid particles especially on the organic materials and clays through cationic exchange, mainly through polyvalent cation bridge [35]. In the present study, the detailed adsorption process is not specified and the adsorption of nitrobenzene on the organic materials or clays via different processes (including polyvalent cation bridge) is integrated and attributed to the total roles of organic materials or clays, since all these processes depend on the existence of the organic materials or clays in the solid particles.

The relative contributions of Fe and Mn oxides in the solid particles to the adsorption of nitrobenzene are slightly less than those of organic materials. Fe and Mn oxides in the solid particles have a greater potential for adsorption of organic compounds and the organic compounds can immobilize in the particles and further transform through complexation with the complex groups on the surface of Fe and Mn oxides or hydrated oxides [36]. The organic pollutants can be adsorbed on Fe oxides not only via surface electrostatic attraction, but also via surface complexation [37]. But no matter which process is primarily responsible for the adsorption of nitrobenzene, Fe oxides in the particles are the most effective components for the adsorption of nitrobenzene and the removal of Fe oxides reduces the amount of the adsorbed nitrobenzene.

Compared with Fe and Mn oxides, contribution of residues to adsorption of solid particles is relatively lower but not negligible, because residues contain a small amount of clay minerals, which have the greatest potential for adsorption of organic compounds due to their large surface area [21,38]. As Fe/Mn oxides and organic materials coated on the surface of residues, the contribution of the residues to nitrobenzene adsorption may be less as shown in the calculated results (about 21 and 13 $\mu\text{g/g}$ particles for surficial sediments and surface coatings, respectively). When residues are separated from the particles and employed to adsorb nitrobenzene, it can be found that the contribution of residues is greater than the calculated value as shown in Table 3 (323 and 403 $\mu\text{g/g}$ particles respectively for the surficial sediments and surface coatings). This result is partly due to the interactions between Fe/Mn oxides and organic materials and residues as shown in Fig. 2. It can be found that the surface of residues after removal of Fe/Mn oxides and organic materials is obviously more cleaned, implying that the Fe/Mn oxides and organic materials either coat or disperse between the residues and thus reduces the surface sites of nitrobenzene reacted with residues, which causes that the calculated amount is much lower than the experimental ones.

The adsorption properties of Fe oxides, Mn oxides, organic materials and residues based on the same basis, i.e. without considering the effect of the relative concentration of each component are also shown in Table 4. It can be found that the adsorption capacity of residues calculated is much lower than that of Fe oxides or organic materials. And even for the adsorption capacities of residues determined by adsorption experiment which is much higher than the calculated value (Table 3), the adsorption potential was still two orders of magnitude lower than those of Fe oxides and organic materials. These results imply that the adsorption capacities of residues are negligible compared with those of Fe oxides and

Table 4
Contribution and sorption capacity of Fe oxides, Mn oxides, organic materials and residues in the solid particles calculated by addition model.

Samples		Fe	Mn	Organic materials	Residues
Surficial sediments	Sorption capacity of each component (Γ) (mg/g component)	26.76	277.24	15.05	0.022
	Langmuir equilibrium coefficient (K) (L/mg)	0.051	0.046	0.061	0.098
	Contribution to nitrobenzene adsorption (C) ($\mu\text{g/g}$ particles)	280.01	148.78	287.88	21.35
	Sorption capacity of each component (Γ) (g/mol component)	1.49	15.23	0.18	–
Surface coatings	Sorption capacity of each component (Γ) (mg/g component)	27.05	360.56	10.61	0.014
	Langmuir equilibrium coefficient (K) (L/mg)	0.045	0.063	0.054	0.073
	Contribution to nitrobenzene adsorption (C) ($\mu\text{g/g}$ particles)	308.29	215.15	513.51	13.15
	Sorption capacity of each component (Γ) (g/mol component)	1.51	19.81	0.13	–

organic materials on a unit mass basis, and the adsorption capacity of Fe oxides is slightly greater than that of organic materials. The adsorption potential of Mn oxides is the highest among the components, and approximately one order of magnitude greater than that of Fe oxides. This result agrees well with the adsorption capacity of each component in the solid particles for heavy metal adsorption as the greatest contribution to Cu or Zn binding to the surficial sediments and surface coatings on a unit mass basis was also attributed to Mn oxides [27]. Compared with the residues, the adsorption potential of clay minerals further separated from the residues significantly increases and that of silicate minerals slightly decreases (Table 3). But compared with Mn oxides, and even if Fe oxides and organic materials, the adsorption capacity of the clay minerals is relatively lower, suggesting that the adsorption capacity of the clay minerals and silicate minerals is negligible as compared with that of Fe/Mn oxides and organic materials. So in the following, in order to compare the adsorption properties of the three most important geochemical components on a molar basis, Γ (mg g⁻¹ component) are transformed into the forms of Γ (mg mol⁻¹ component) (Table 4). As shown in Table 4, the adsorption capacity of nitrobenzene on each of the three components follows the order of Mn oxides > Fe oxides > organic materials. The adsorption capacity of Mn oxides is about an order of magnitude greater than that of Fe oxides and nearly two orders of magnitude greater than that of organic materials, respectively, revealing that Fe and Mn oxides are more important than organic materials for nitrobenzene adsorption on the solid particles. This angle of vision, the point of view from which the adsorption ability of solid particles is divided into several fractions, is different from that in the previous studies reported in the literature and provides a new method to investigate reactions between organic pollutants and solid particles.

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