Selective extraction and separation of Fe, Mn oxides and organic materials in river surficial sediments

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Abstract: In order to investigate the adsorption mechanism of trace metals to surficial sediments (SSs), a selective extraction procedure was improved in the present work. The selective extraction procedure has been proved to selectively remove and separate Fe, Mn oxides and organic materials (OMs) in the non-residual fraction from the SSs collected in Songhua River, China. After screening different kinds of conventional extractants of Fe and Mn oxides and OMs used for separation of heavy metals in the soils and sediments, $NH_2OH \cdot HCl$ (0.1 mol/L) + HNO_3 (0.1 mol/L), $(NH_4)_2C_2O_4$ (0.2 mol/L) + $H_2C_2O_4$ (pH 3.0), and 30% of H_2O_2 were respectively applied to selectively extract Mn oxides, Fe/Mn oxides and OMs. After the extraction treatments, the target components were removed with extraction efficiencies between 86.09%—93.36% for the hydroxylamine hydrochloride treatment, 80.63%—101.09% for the oxalate solution extraction, and 94.76%—102.83% for the hydrogen peroxide digestion, respectively. The results indicate that this selective extraction technology was effective for the extraction and separation of Fe, Mn oxides and OMs in the SSs, and important for further mechanism study of trace metal adsorption onto SSs.

Keywords: surficial sediments; selective extraction; iron oxides; manganese oxides; organic materials

Introduction

Heavy metals contained in suspended solids of water column could be entrapped into the surficial sediments (SSs) during the sedimentation processes, and then the SSs would be contaminated by the accumulation of heavy metals and other pollutants through various reactions such as ionic exchange, complexation with organic substances, or incorporation with sediments (Yu *et al.*, 1996; Chartier *et al.*, 2000). SSs received the pollutants from the anthropogenic activities, industrial and urban wastes inevitably discharged into water bodies, and act as both carriers and potential sources of contaminants in an aquatic environment because heavy metals are permanently held by them and can be released back into the water bodies (Pardo *et al.*, 1990; Dudka and Adriano, 1997; Arribére *et al.*, 2003; Hong *et al.*, 2003). So, the SSs in rivers plays an important role in influencing water quality in the river systems and heavy metals in SSs have drawn great interest due to the toxicity and bioaccumulation potential of them (Vuceta and Morgan, 1978; Lion *et al.*, 1988; Santschi *et al.*, 1997; Farag *et al.*, 1998; Jain and Sharma, 2001).

The presence of heavy metals in SSs is partly affected by the composition of sediments (Combest, 1991; Sabri *et al.*, 1993; Jain and Sharma, 2001). As compared with other components in the SSs, Fe, Mn oxides and organic materials (OMs) are crucial for the binding and sorption of heavy metals related to their abundance (Lion *et al.*, 1982, 1988; Byran and Langston, 1992; Young and Harvey, 1992; Perret *et al.*, 2000; Turner, 2000; Turner *et al.*, 2004). In order

to understand the relative importance of Fe oxides, Mn oxides and OMs in controlling metals adsorption and provide a chemical understanding of the underlying adsorption mechanisms, researches have combined the chemical extraction of sorbent phases such as metal oxides and OMs, with uptake of trace metals by the remaining, digested particles (Lion *et al.*, 1982; Fujiyoshi *et al.*, 1994; Dong *et al.*, 2000, 2002, 2003). But the chemical extractions employed in these studies are neither completely selective nor specific except for the use of extractions in the natural surface coatings (NSCs) by Dong *et al.* (2000, 2002, 2003). And that only the selective extraction technology combined with additive-adsorption and linear-regression models could provide an effective method to quantitatively investigate the roles of metal oxides and OMs in controlling the sorptive behaviors of heavy metals. Therefore, in order to apply the additive-adsorption and linear-regression models to explain the underlying mechanisms of heavy metals adsorption to the sediments, the selective chemical extraction procedure, which was suitable for the SSs, should be developed and perfected renewably because the SSs were more or less different from the NSCs in composition.

The purpose of the present study was to develop and improve a selective chemical extraction procedure based on the previous studies to selectively remove Fe, Mn oxides and OMs from SSs for the further research on metals adsorption mechanisms.

1 Materials and methods

1.1 Collection and characterization of SSs

Four sampling locations in this study were selected along the shore of Songhua River that meandering through the Jilin City, China, an industrial city located in the upstream of the Songhua River. The sampling locations were named as Linjiangmen Bridge (S1), Jilin Bridge (S2), Hongbin Bridge (S3) and Longtan Bridge (S4), and SSs samples were taken downstream.

The SSs (approximately 5 cm in depth from the surface) were collected with a plastic scoop and stored in polyethylene bags. During collection of the SSs, 4 sub-samples approximately 20 cm from each other in distance were obtained and mixed into one homogeneous sample in each sampling location. Then the SSs samples were transported to the laboratory and dumped into plastic containers in which contain minimal mineral salts (MMS) solution (Table 1). Prior to sampling, the plastic scoop and containers were pre-cleaned with detergent, soaked for 24 h in soap solution, acid washed for 24 h in 6:1 (v/v) of H_2O: HNO_3, and then rinsed in distilled-deionized water (ddH$_2$O), followed by a second 24 h acid wash and a final rinse in ddH$_2$O. The samples were pretreated with sieving to remove the debris and settling to separate the sand and gravel. The treated samples were then preserved at 4℃ in MMS solution.

OMs expressed as total organic carbon (TOC) in the SSs was determined by "oxidative combustion-infrared analysis" method and measured by a TOC-analyzer(TOC-VCPH, Shimadzu, Japan); Pseudototal amounts of Fe and Mn were digested by HCl-HNO$_3$-HClO$_4$, and the metals in supernatant were measured by a WYX-9004 flame atomic absorption spectrometer (FAAS) equipped with a SML-III graphite furnace (Shenyang, China). Distilled-deionized water (ddH$_2$O) was used through the study. All glassware and other containers were thoroughly cleaned and finally rinsed with ddH$_2$O prior to use.

Table 1 Composition of MMS solution used in the pretreatment and preservation of SSs

	Component	Concentration, μmol/L	Concentration, mg/L
MMS medium	CaCl$_2$·2H$_2$O	200	30
	MgSO$_4$·7H$_2$O	140	35
	(NH$_4$)$_2$SO$_4$	910	120
	KNO$_3$	150	15
	NaHCO$_3$	10	0.84
	KH$_2$PO$_4$	5	0.70

Note: MMS. minimal mineral salts

1.2 Selective extraction procedure

The extraction techniques employed in this study were modifications of those from Agbenin and Olojo

(2004) and Dong *et al.* (2002, 2003). The SSs were extracted with three different extraction reagents in isolation to remove target components. Extraction with 0.1 mol/L NH$_2$OH·HCl + 0.1 mol/L HNO$_3$ for 30 min was undertaken to remove manganese oxides, instead of extraction with 0.02 mol/L NH$_2$OH·HCl + 0.01 mol/L HNO$_3$ for 20 min as used by Dong *et al.* (2002, 2003). The differences between surficial sediments and natural surface coatings in the main chemical characteristics, such as manganese oxides, iron oxides and organic materials were obviously observed. On the other hand, extraction with 0.02 mol/L NH$_2$OH·HCl + 0.01 mol/L HNO$_3$ for 20 min was proved to be not suitable for selective extraction of manganese oxides in SSs and failed in extraction of manganese oxides in SSs with higher extraction efficiency, although it has been succeeded in selectively extraction of manganese oxides in natural surface coatings. So, the concentrations of NH$_2$OH·HCl and HNO$_3$ were all increased to 0.1 mol/L to improve the extraction efficiency of manganese oxides. In the former experiments of this study, 0.3 mol/L Na$_2$S$_2$O$_4$ (pH 6.0) extraction for 40 min was used to digest iron and manganese oxides simultaneously (Dong *et al.*, 2002, 2003). But the results indicated that S$_2$O$_4^{2-}$, as well as the decomposed products of S$_2$O$_4^{2-}$ interfere the analysis of extraction solution. So, a solution of 0.2 mol/L (NH$_4$)$_2$C$_2$O$_4$ buffered at pH 3.0 with H$_2$C$_2$O$_4$ and shaken in the dark for 4 h was directly used as a reference from Agbenin and Olojo (2004) to digest both Fe and Mn hydrous oxides. The extraction result indicated that 0.2 mol/L (NH$_4$)$_2$C$_2$O$_4$ (pH 3.0) was good at digesting iron and manganese oxides with higher extraction efficiency and the effect on organic materials was negligible. Extraction with 3.0 ml H$_2$O$_2$ (30%) heating on a hot plate was conducted to remove OMs, as compared with the use of 1.5 ml H$_2$O$_2$ (60%) heating on a hot plate by Agbenin and Olojo (2004).

These extractions were taken in 50-ml polyethylene centrifugal tubes, and all the reagents in the extraction processes were in trace metal grades. The details of extraction processes were as the following.

Selective removal of OMs: Before extraction, SSs preserved in MMS solution were homogenized by magnetic stirring. Then suspending material of 10 ml (approximately 0.25 g) was transferred to 50-ml polyethylene centrifugal tubes in triplicate. The samples were centrifuged at 3800 r/min and clear supernatant solutions were carefully discarded to avoid loss of particles. 3.0 ml of hydrogen peroxide (30%) was added to the sediment in the centrifugal tubes. The centrifuge tubes were placed in a 500-ml capacity beaker filled to the 150 ml mark with water and preheated to a boiling point on a hot plate. Heating was stopped after the sediment suspensions

boiled for 20 min, and the suspensions were allowed to cool for 40 min. The particles were washed thrice with MMS solution of 20 ml and shaken for 30 min. The sediment suspensions were centrifuged again at 3800 r/min and clear supernatant solutions were carefully decanted to 100 ml volumetric flasks to avoid loss of particles. The sediment in the centrifugal tubes in which OMs were not destroyed was also washed thrice with MMS solution to serve as a reference condition for calculating the efficiency of selective removal of OMs. The sediment samples in tubes after the above treatment were air-dried for the measurement of TOC. The solutions in the 100 ml volumetric flask were used for determination of Fe and Mn extracted.

Selective removal of Mn: as described in the removal of OMs, sediment samples of equal-quantity were also obtained by centrifuging at 3800 r/min in quintuplicate. The mixture of $NH_2OH \cdot HCl$ (0.1 mol/L) + HNO_3 (0.1 mol/L) was used to remove manganese oxides only 20 ml $NH_2OH \cdot HCl$ solution was added to tubes. The sediments in the tubes were then shaken for 30 min. Excess hydroxylamine hydrochloride in the sediment was removed by washing thrice with MMS solution following by shaking for 30 min. The sediments were centrifuged at 3800 r/min and clear supernatant filtered into 100 ml volumetric flask for the determination of Mn. The sediment samples in tubes after the hydroxylamine hydrochloride treatment were also air-dried for the determination of TOC.

Both Fe and Mn removal: similarly, sediment samples of equal-quantity were also put in the centrifugal tubes and extracted with an oxalate solution buffered at pH 3.0 and shaken in dark for 4 h to remove both Fe and Mn oxides. After extraction, excess oxalate solution was also removed by washing thrice with MMS solution following by shaking for 30 min. The clear supernatant solutions were used for measurement of Fe and Mn and the remains of sediments in the tubes were used for determination of TOC.

Previously, some authors suggested that Fe and Mn in the SSs could be defined as two fractions by using sequential extraction procedure, i.e. non-residual fraction (also called total extractable fractions, including five binding phases of exchangeable, bound to carbonates, bound to Mn and Fe oxides and to OMs) and residual fraction. In this study, the total extractable amounts of Fe and Mn in the SSs were determined by using the modified sequential extraction procedure (MSEP) (Belzile et al., 1989; Tessier et al., 1989; Yu et al., 2001) (Table 2). Furthermore, some studies indicated that determining total contents of heavy metals in SSs was insufficient to assess the environmental impact of

heavy metals on the environment or organism (Ma and Rao, 1997; Mester et al., 1998; Barona et al., 1999); they suggested that metals associated with the residual fraction in soils or SSs samples should be highly unavailable to organism. Hence, the Fe and Mn oxides in the non-residual fraction of SSs were defined as the total Fe and Mn oxides for the convenience of calculating the efficiency of selective extraction for Fe and Mn oxides in the SSs, and those in the residual fraction were negligible. Meanwhile, the total extractable OMs amount was also determined by using the MSEP in consistent with the efficiency calculation of Fe and Mn oxides extraction.

Table 2 Conditions employed in the MSEP to determine the total extractable amount of Fe and Mn oxides and OMs

Fraction	Extracting reagent	Shaking time, h	Temp., °C
Exchangeable	1 mol/L $MgCl_2$ (pH 7.0)	0.5	25±2
Bound to carbonates	1 mol/L CH_3COONa (pH 5.0, HOAc)	5	25±2
Bound to Mn oxides	0.1 mol/L $NH_2OH \cdot HCl$+0.1 mol/L HNO_3	0.5	25±2
Bound to Fe oxides	0.04 mol/L $NH_2OH \cdot HCl$+25% HOAc(v/v)	6	96±2
Bound to OMs	0.1 mol/L HNO_3+30% H_2O_2 (pH 2.0, HNO_3)	5	85±2
Residual	HNO_3-HCl+$HClO_4$		

In this study, in order to investigate the stability of the above extraction methods for the separation of Fe, Mn oxides and OMs in the SSs, each sample of sediments sampled in different locations or pretreated with different pretreatments was conducted in quinary and the standard deviation of repeated conduction of the method based on the same experimental conditions was calculated. And that in order to investigate the applicability of the above extraction methods for the separation of Fe, Mn oxides and OMs in the SSs, samples with different pretreatment were exposed to the extraction agents, which were collected in the same sampling location. The sample with air-drying and sieving treatment was labeled as S1* which was sampled in the summer of 2004 in the location of Linjiangmen Bridge, and the sample with preservation at 4°C in MMS solution was labeled as S1 which was sampled in the summer of 2005 in the same sampling location. Meanwhile, four samples with the same pretreatment were collected in the different sampling locations at the same time in 2005 to further investigate the applicability of the extraction technology used in this study.

2 Results and discussion

2.1 Characteristics of the surficial sediments

Initial characteristics of the SSs samples are shown in Table 3. The OMs contents of the sediments collected in 2005 expressed as TOC ranged from 1845.48 to 2281.16 μmol C/g; the concentration of pseudo-total Fe oxides was about 35 time greater than that of pseudo-total Mn oxides in average. The Fe, Mn and OMs from sediments sampled in location S4 were all slightly more than those of the other three locations, and those of S2 were the least among the four samples.

The total extractable contents of Fe oxides

Table 3 Total extractable amounts of Fe and Mn oxides and OMs in the SSs determined by MSEP

Location		Fe oxides[a], μmol Fe/g	Mn oxides[a], μmol Mn/g	OMs[b], μmol C/g
S1*	Pseudo-total amount	437.65±6.71	7.32±0.29	1049.91±110.45
	Total extractable amount	83.68±2.23	3.99±54.51	273.11±11.21
	Extractable percentage	19.12%	54.51%	73.99%
S1	Pseudo-total amount	352.28±7.43	9.27±0.27	2031.20±16.38
	Total extractable amount	153.70±2.26	6.47±0.14	335.62±14.20
	Extractable percentage	43.63%	69.79%	83.48%
S2	Pseudo-total amount	266.20±4.20	8.32±0.31	1845.48±12.36
	Total extractable amount	117.37±1.04	5.84±0.27	318.60±13.99
	Extractable percentage	44.09%	70.12%	82.74%
S3	Pseudo-total amount	337.16±5.61	9.60±0.48	1975.84±3.53
	Total extractable amount	151.56±4.84	7.08±0.38	243.24±17.01
	Extractable percentage	44.95%	73.74%	87.69%
S4	Pseudo-total amount	378.02±5.41	10.66±0.43	2387.30±63.58
	Total extractable amount	175.91±3.55	8.35±0.27	255.20±19.59
	Extractable percentage	46.53%	78.31%	88.81%

Notes: [a] Mean(n=5)±SD and the concentration was the extracted amount; [b] mean (n=3)±SD and the concentration was the TOC amount of the remaining, digested sediments

ranged from 117.37 to 175.91 μmol Fe/g and those of Mn oxides were with a range of 5.84 to 8.35 μmol Mn/g, respectively, which was equivalent to the pseudo-total Fe and Mn oxides contents of about 45% and 70% in average. These results indicate that Fe and Mn in residual fractions shared a considerable part of the pseudo-total Fe and Mn oxides in the sediments. In the present study, the total extractable content of OMs was also determined by MSEP and a large part of OMs in the SSs was removed by MSEP treatment with a range of 83.48% to 88.81%.

For the sample S1*, which was collected in July 2004 and pretreated with air-drying and grounding through a mortar, and of which particles larger than 0.076 mm were discarded by sieving, the OMs content was 1049.91 μmol C/g and approximately on a half of the sample S1. The pseudo-total Fe and Mn oxides contents of S1* were 437.65 μmol Fe/g and 7.32 μmol Mn/g respectively, being slightly different from the S1. This result was partly due to the difference of sampling time, as well as the difference of sample pretreatments. Stone and Droppo (1996) reported that metal partitioning in different size fractions varied clearly. Compared to S1, the extractable contents of

Fe, Mn and OMs in S1* were all lower, especially for Fe, and only 19.12% of the pseudo-total Fe was digested by the first five steps of MSEP. This implied that the treatment with air-drying obviously decreased the extractability of Fe, Mn and OMs in the SSs.

2.2 Effect of sample pretreatment on extraction efficiencies

In the previous studies on the natural surface coatings (NSCs), hydrogen peroxide combined with nitric acid was always used to remove OMs. However, this extraction treatment may also remove sulphide minerals and partially digest easily reducible Mn oxides if not used after sample treatment with a reducing agent (Chao, 1984). We therefore directly applied H_2O_2 as the extraction agent for the OMs removal without the addition of acid in the present study. The results of SSs extracted with H_2O_2 heating on a hot plate are listed in Table 4. It could be found that the removal efficiencies of OMs by hydrogen peroxide treatment reached 94.76% and 98.99% for S1* and S1 respectively, implying that for the target component, hydrogen peroxide was an effective extraction reagent for OMs removal not only for the sample preserved in MMS solution, but also for the

sample pretreated by air-drying. In comparison, only 0.31% and 2.95% of Fe was removed from S1* and S1, this reached the purpose of selective removal of OMs. However, for the other non-target component Mn, the effect of hydrogen peroxide extraction was greater than that on Fe, especially for the sample pretreated by air-drying and the removal of Mn by this extraction reagent reached 33.05% for S1*, but only

8.50% for S1. These results indicated that extraction with hydrogen peroxide heating on a hot plate to selective remove OMs was more effective for the sample preserved in MMS solution (S1) than for the sample pretreated by air-drying (S1*), and hydrogen peroxide can be efficiently employed in the selective extraction of OMs from the SSs sample preserved in MMS.

Table 4   Assessment of removal of Fe and Mn oxides and OMs in the SSs by selective extractions

Location	Extractant	Fe oxides[a]		Mn oxides[a]		OMs[b]	
		Concentration, μmol Fe/g	Removal, %	Concentration, μmol Mn/g	Removal, %	Concentration, μmol C/g	Removal, %
S1*	NH$_2$OH·HCl extraction	18.49±2.03	22.09±2.43	2.52±0.55	63.15±13.78	1014.32±103.11	4.58±0.46
	H$_2$O$_2$ extraction	0.26±0.30	0.31±0.36	1.32±0.16	33.05±4.01	313.82±12.17	94.76±3.67
	Oxalate extraction	81.66±4.42	97.59±5.28	3.64±0.08	91.30±2.01	1005.71±85.75	5.69±0.48
S1	NH$_2$OH·HCl extraction	30.80±1.32	20.04±0.86	5.57±0.05	86.09±0.77	2013.22±23.75	1.06±0.01
	H$_2$O$_2$ extraction	4.54±0.32	2.95±0.21	0.05±0.05	8.50±8.50	352.70±15.53	98.99±4.36
	Oxalate extraction	132.12±1.50	85.96±0.98	5.88±0.08	90.88±1.24	2025.60±0.42	0.33±6.84
S2	NH$_2$OH·HCl	19.66±0.26	16.75±0.22	5.22±0.09	89.38±1.54	1773.90±11.96	4.69±0.03
	H$_2$O$_2$ extraction	4.36±0.04	3.71±0.03	0.61±0.03	10.45±0.51	275.39±12.40	102.83±4.63
	Oxalate extraction	118.65±1.68	101.09±1.43	5.29±0.09	90.58±1.54	1812.31±36.76	2.17±0.04
S3	NH$_2$OH·HCl extraction	28.97±1.54	19.11±1.01	6.61±0.06	93.36±0.85	1934.79±94.94	2.37±0.12
	H$_2$O$_2$ extraction	7.20±0.49	4.75±0.32	0.88±0.05	12.43±0.71	250.29±43.53	99.59±17.32
	Oxalate extraction	122.21±3.55	80.63±2.34	6.86±0.09	96.89±1.27	1967.04±11.07	0.51±0.01
S4	NH$_2$OH·HCl extraction	30.04±1.58	17.08±0.89	7.51±0.09	89.94±1.08	2346.34±68.62	1.92±0.05
	H$_2$O$_2$ extraction	6.13±0.94	3.48±0.53	1.04±0.10	12.46±1.19	290.02±6.09	98.37±2.06
	Oxalate extraction	148.46±2.59	84.40±1.47	7.71±0.18	92.34±2.15	2381.16±66.52	0.29±0.01
Standard deviation	NH$_2$OH·HCl extraction	1.59%		2.98%		1.55%	
	H$_2$O$_2$ extraction	0.76%		1.89%		1.99%	
	Oxalate extraction	8.99%		2.91%		0.90%	

Notes: [a] Mean (n=5) ±SD and the concentration was the extracted amount; [b] mean (n=3)±SD and the concentration was the TOC amount of the remaining, digested sediments

A number of reagents have been used to selectively remove either Mn oxides or amorphous Fe oxides or both (Chao and Zhou, 1983; Chao, 1984), but one of the most popular reagent which has been applied to digest Mn oxides only is a combination of reducing agent (0.01—0.1 mol/L NH$_2$OH·HCl) and a dilute nitric acid (0.01—0.1 mol/L HNO$_3$) which was originally used in sequential extraction procedure for the speciation of particulate trace metals (Belzile et al., 1989; Yu et al., 2001), then widely used in partial extraction for qualitative analysis of the relative importance of Mn oxides in binding of trace metals (Young and Harvey, 1992), or in the selective extraction for distinguishing the specifically adsorbed heavy metals (Keller and Védy, 1994). Now it was developed to selectively remove Mn oxides from the

NSCs and then combine the selective chemical extraction of sorbent phases such as, Mn oxides, Fe oxides and OMs, with the adsorption of trace metals by the remaining, digested NSCs to quantitatively determine the role of Mn oxides on the uptake of trace metals (Dong et al., 2000, 2002, 2003). In this study, the mixture of NH$_2$OH·HCl (0.1 mol/L) + HNO$_3$ (0.1 mol/L) was used to extract easily reducible Mn oxides only. The extraction results for the NH$_2$OH·HCl treatment are also summarized in Table 4. The results showed that the removal efficiency of Mn oxides reached 86.09% for S1; the effect of the extraction treatment on OMs was negligible and only 1.06% of OMs was digested by this extraction agent. However, the NH$_2$OH·HCl extraction released only 63.15% of Mn oxides from the non-residual fraction of S1*,

although the effect of $NH_2OH \cdot HCl$ on the OMs was also negligible. These results may be due to the difference of Mn existed in individual associated phase between S1 and S1*, and Mn existed as easily oxidizable solids/compounds form (bound to OMs) in S1* was more than that in S1 (Table 5); thus Mn bound to this phase was difficult to be removed by extraction with $NH_2OH \cdot HCl$. For the other non-target component Fe, the $NH_2OH \cdot HCl$ extraction digested more than 20% of Fe both from S1 and from S1*. The slightly more Fe oxides were digested in the selective removal of Mn oxides may be due to the digestion of some carbonate minerals. From the results of the

MSEP, it could be found that about 20% of total extractable Fe in the S1 and 10% in the S1* were existed as carbonatic phase (Table 5). So the slightly more Fe extracted in the selective removal process of Mn oxides was acceptable and the combination of 0.1 mol/L $NH_2OH \cdot HCl$ and 0.1 mol/L HNO_3 was proved to be an alternative approach to selective remove Mn oxides from the sample preserved in MMS solution (S1), and the applicability of this reagent to the sample pretreated with air-drying (S1*) was slightly unsatisfactory.

As described above, a number of chemical agents have been employed to selectively extract either Mn

Table 5 Fractions of Fe and Mn oxides in the SSs determined by MSEP

	S1*		S1		S2		S3		S4	
	Fe, %	Mn, %	Fe, %	Mn, %	Fe, %	Mn, %	Fe, %	Mn, %	Fe, %	Mn, %
Exchangeable	0.00	0.61	0.14	6.38	0.88	5.32	0.55	5.48	0.10	4.71
Bound to carbonates	0.06	4.47	6.60	15.67	11.03	17.66	10.03	14.46	11.83	16.25
Bound to Mn oxides	0.80	26.61	9.10	31.31	7.53	32.38	8.27	39.84	6.37	40.99
Bound to Fe oxides	16.15	16.82	25.75	13.10	22.56	12.18	23.58	11.11	25.44	13.16
Bound to OM	2.12	5.81	2.04	3.33	2.09	2.58	2.53	2.85	2.80	3.21
Residual	80.88	45.41	56.37	30.21	55.91	29.88	55.05	26.26	53.47	21.69

oxides or amorphous Fe oxides or both. Oxalate buffer solution was a representative reagent to extract both amorphous Fe and Mn oxides. Similar to $NH_2OH \cdot HCl$, the mixture of $(NH_4)_2C_2O_4$ and $H_2C_2O_4$ in different proportions was also used in sequential extraction (Ma and Uren, 1998) or selective extraction (Agbenin and Olojo, 2004) of the particles. In the present study, extraction with 0.2 mol/L $(NH_4)_2C_2O_4$ buffered at pH 3.0 with $H_2C_2O_4$ and shaken in the dark for 4 h was conducted to remove Fe and Mn oxides; meanwhile, the effect on the OMs removal was expected to be negligible. It could be found in Table 4 that the removal of target components Fe and Mn oxides were satisfactory and the removal efficiencies were all more than 85% both for S1 and S1*. And that for the non-target component OMs, the effect of oxalate extraction was negligible and only 0.33% of OMs for S1 and 5.69% for S1* were digested. These results implied that 0.2 mol/L $(NH_4)_2C_2O_4$ (pH 3.0) used as the selective extraction agent for both Fe and Mn oxides in the non-residual fraction of SSs was feasible for the further mechanism investigation of metals adsorption onto SSs.

In general, the extraction method in this study was an alternative approach to selective remove Mn oxides, Fe oxides and OMs from SSs sample preserved in MMS solution (S1), and the applicability of this extraction technology to the sample pretreated with air-drying (S1*) was slightly unsatisfactory.

2.3 Selective extraction of Fe, Mn oxides and OMs

In order to examine the applicability and stability of this extraction technology and further investigate mechanisms of metals adsorption onto SSs, four SSs samples (S1, S2, S3 and S4) collected at the same time in the different sampling locations were exposed to the extraction agents and the results are also shown in Table 4.

It could be found that the removal efficiencies of OMs by hydrogen peroxide treatment reached 94.76% —102.83%; the effects of the extraction treatment on Fe oxides were negligible (2.95% —4.75% of Fe oxides were digested by H_2O_2). However, the effects on Mn oxides were greater than those on Fe oxides and the extraction efficiencies of Mn oxides were within a range of 8.50%—10.46%. This may be due to the binding form of Mn to the SSs, and considerable part of Mn in the SSs was existed as exchangeable and carbonates forms; thus Mn bound to these phases was easily extracted by the water after the H_2O_2 treatment. In general, H_2O_2 can be efficiently employed in the selective removal of OMs from the SSs. The $NH_2OH \cdot HCl$ extraction released 5.22—7.51 µmol Mn/g from the non-residual fraction of the SSs, which were equivalent to the total extractable Mn content of about 86.09% —93.36%, and only 0.89% —3.88% of OMs were digested. These results implied that hydro-xylamine hydrochloride was valid for the selective

removal of Mn oxides from the SSs if only considering Mn oxides and OMs. The extraction of this reagent removed in excess of 20% of the total extractable Fe oxides, this was slightly out of expectation. The extraction efficiencies of oxalate buffer solution for Fe oxides were between 80.63% — 101.09% and those for Mn oxides were ranged from 90.58% to 96.89%. Only less than 1.80% of OMs was digested from the SSs, implying that the effects on non-target components were negligible. These results indicated that 0.2 mol/L $(NH_4)_2C_2O_4$ (pH 3.0) used as the selective extraction agent for both Fe and Mn oxides in the non-residual fraction of SSs was feasible.

In Table 4, it could be also found that for the samples collected in different sampling locations, the standard deviation of extraction efficiencies of Mn oxides with $NH_2OH \cdot HCl$ extraction was 2.98%, and that of OMs with H_2O_2 treatment was also only 1.99%. However, the standard deviation of extraction efficiencies of Fe oxides with oxalate buffer solution treatment was almost up to 8.99%, although that of Mn oxides was only 2.91% . The slightly higher standard deviation of extraction efficiencies for Fe oxides treated with oxalate buffer solution was due to the higher extraction efficiency of Fe oxides in S2, and this effect was partly positive because it improved the extraction efficiency. So, the selective extraction technology used in this study had a good reappearance and stability, and it can be used widely in SSs. The results also indicated that the applicability of this extraction procedure was more limited for Fe oxides than Mn oxides and OMs.

3 Conclusions

In a conclusion, the following may be drawn based on the results of this study:

(1) A selective extraction technology was developed and proved to be suitable for the separation of Fe oxides, Mn oxides and OMs in the SSs collected in the Songhua River.

(2) The extraction reagents of $NH_2OH \cdot HCl$ (0.1 mol/L) + HNO_3 (0.1 mol/L), $(NH_4)_2C_2O_4$ (0.2 mol/L) + $H_2C_2O_4$ (pH 3.0), and 30% of H_2O_2 were respectively proved to selectively extract Mn oxides, Fe/Mn oxides and OMs with extraction efficiencies of 86.09% — 93.36%, 80.63% — 101.09% and 94.76% — 102.83%. The results indicate that Mn oxides, Fe oxides and organic materials in non-residual fraction of surficial sediments were all suitable to be exposed to this technology and organic materials were more suitable.

(3) The establishment of this selective extraction technology made a good preparation for determining the relative importance of metal oxides and OMs in aquatic environments, during the adsorption process of trace metals onto SSs. This approach avoids the complex computing model and the effect of

interaction among the components on the adsorption, which have to be faced if trace metals adsorption is operated before the separation. Further research will be focused on in ternal and external metals adsorption mechanisms in SSs using the selective extraction technology.

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