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FRACTION OF HEAVY METALS IN SLUDGES FROM TYPICAL COKING WASTEWATER TREATMENT PLANTS BY MODIFIED BCR SEQUENTIAL EXTRACTION PROCEDURE

Fractions of 8 heavy metals (Cd, Cr, Hg, Cu, Zn, Pb, Ni and As) in sludges from two typical coking wastewater treatment plants were determined by atomic absorption spectroscopy (AAS) using the modified the European Community Bureau of Reference sequential extraction procedure as the pretreatment technology. The sludges from biological, coagulation deposition units and the discharged sludges of two plants were sampled and the exchangeable, reducible, oxidable, residual fraction and the total content were determined. The oxidable or residual fraction was the predominant fraction in various sludges and on the contrary that the values of the exchangeable and reducible fractions were much lower. Poor biological availability and low potential environment risk of heavy metals was found in sludges from typical coking wastewater treatment plants. Further results of cluster analysis conducted by SPSS that the units with similar conditions could be classed together identified that the unit condition was one key factor affecting on the fraction of heavy metals in sludges.

1. INTRODUCTION

Heavy metals are concerned contaminants due to the high toxicity and nonbiodegradability. The speciation of heavy metals determined the biodegradability and the toxicity [1, 2]. Many factors could affect the speciation of metals such as pH, concentration of sulfide and inorganic phosphate in soil and sludge [3]. In order to assess the toxicity of heavy metals in sludge or soil, heavy metals should be divided into different speciation based on the mobility of heavy metals in soil or sludge.

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Different speciation of heavy metals in soil, sludge and sediment is distinguished by means of specific solvents [4]. Based on different solvents, numerous methods were proposed to assess the actual toxicity of heavy metals [5–7]. Among these methods, the two most widely used are the Kersten–Forstner and Tessier procedures. Many authors reported extraction of a fraction of heavy metals in soil and sediment employing the Kersten–Forstner, and especially Tessier procedure [8–12]. Although a lot of methods have been used to determine the speciation of heavy metals in solid samples, the results are difficult to compare because of different solvents used to extraction. The European Community Bureau of Reference (BCR) introduced the criteria for the speciation of heavy metals in solid samples as a standard sequential extraction, and modification introduced subsequently. The modified BCR method with based on the exchangeable, reducible, oxidable and residual speciation is now the most commonly used sequential extraction procedure for speciation of heavy metals in solid samples [13–16].

Heavy metals are abundant in wastewater and are mainly removed by adsorption to activated sludge during the treatment process. Lasheen conducted the analysis of heavy metals in sludges from six wastewater treatment plants in Egypt. Lasheen and Ammar [17] found that Mn, Ni and Zn showed great degree of mobility in the sludges, and simultaneously Cr, Cu, Cd and Fe were not mobilized. Alonso et al. [18] investigated Al, Cd, Co, Cu, Cr, Fe, Mn, Hg, Mo, Ni, Pb, Ti and Zn fractions in the sludge of wastewater treatment, and the results showed clear increase of mobility of heavy metals during the sludge treatment process. This research [18] contributed to the assessment of the potential environmental and health risk associated with the sludge coming from wastewater treatment plants. Wang et al. [19] studied the fraction of heavy metals in sludge from wastewater treatment plants, and the factors affecting the speciation were selected. The results showed that the content of organic matter, total phosphorus and total nitrogen of sludge exhibited a significant positive correlation with the content of exchangeable and reducible of Pb, Mo, Cr, Cu, and Fe. However, the speciation analysis of heavy metals in sludge was mainly conducted for the sewage treatment plants and heavy metal fraction in sludge from industrial wastewater treatment plants rarely have been reported. The fraction of heavy metals from sewage and industrial wastewater treatment plants probably differ from each other due to the different characteristic of the raw wastewater and the treatment technology. Therefore, it is necessary to investigate the fraction of heavy metals in sludges from industrial wastewater treatment plants.

Coking wastewater originates from the coke refining process whose product is the necessary material for steelmaking. Many heavy metals are present in coal and the refining process is an important pollution source [20, 21]. Moreover, Cu, Mn, Zn, Ni, Pb, Cd and As were proved be in the coking wastewater by Ren [22]. Up to now, the most widely used treatment technologies for coking wastewater are biological ones. Heavy metals are adsorbed by activated sludge during the treatment process, and the fraction of heavy metals determined the potential environmental and health risk of the produced sludge. Hence that it is necessary to analyze the fraction of heavy metals and the fraction

characteristic of heavy metals in sludges from different treatment units of the coking wastewater treatment plant.

The aims of this work are as follows:

1. To elaborate the fraction characteristic of heavy metals in different units based on different treatment conditions.

2. To demonstrate the factors affecting on the fraction characteristic.

3. To evaluate the potential environment and health risk of the produced sludge during the treatment of coking wastewater.

In order to achieve the aims of this work, the fraction of 8 heavy metals such as Cd, Cr, Hg, Cu, Zn, Pb, Ni and As in different sludges were determined employing the modified four step BCR sequential extraction procedure as pretreatment technology prior to atomic adsorption spectrometry. Arsenic, which is not a heavy metal, was also taken into consideration because its toxicity is similar to that of heavy metals. The sludges were sampled from two typical coking wastewater treatment plants which based on anaerobic/aerobic/aerobic (A/O/O) and anaerobic/aerobic/hydrolysis/aerobic (A/O/H/O) three phase biological fluidized beds, respectively. Moreover, for the first time the mathematical software Statistical Product and Service Solutions (SPSS) was applied for the cluster analysis of the fraction of heavy metals, and the fraction characteristic of heavy metals in sludge was presented.

2. EXPERIMENTAL

Reagents and materials. Stock solutions of 1000 mg·dm^{-3} Cr and 100 mg·dm^{-3} Cd, Hg, Cu, Zn, Pb, Ni, As were purchased from Chinese National Standard Sample Center. Hydrochloric acid, nitric acid, perchloric acid, acetic acid, hydroxylamine hydrochloride were all purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. (Tianjin, China). H_2O_2 (30%), sodium borohydride, ultra pure argon (99.999%) and ethylene were Chemical Reagent Co., Ltd. (Laiyang, China). Crucible tongs, 0.45 µm filter membranes, plastic centrifugation tubes and Erlenmeyer flasks were purchased from Tianjin Fengchuan Chemical Reagent Science and Technology Co., Ltd. (Tianjin, China).

Instrument. The contents of heavy metals in sludges were determined by a Shimadzu AA-6300 atomic adsorption spectrometry (AAS). Electric jacket was used to heat the extraction solvent. QL-40 air compressor was used to provide air for burning. SHZ-D vacuum pump was used to filter the extraction solvent. The samples were weighted using a HR-200 electronic balance. The samples were stored in a KK23V65Tl Siemens refrigerator. THZ-C-1 oscillator was used to extract heavy metals in samples. Anke TDL-5-A centrifugal machine was used to separate the sludge sample and the extraction solvent. HH-2 thermostat water bath was used to maintain constant temperature during extraction.

Wastewater treatment plant and samples. The sludges from two coking wastewater treatment plants located in Shaoguan, Guangdong province in China were collected. The two plants are based on A/O/O and A/O/H/O three phase biological fluidized bed technologies, respectively. For the A/O/O treatment plant, one coagulation unit was placed before the anaerobic (A) unit, and one biological filter unit followed the second aerobic (O) unit. In order to increase the quality of discharged water for the two plants, coagulation unit was placed after the biological treatment. Therefore, for the A/O/O treatment plant, seven sludge samples including the coagulation deposition sludge before biological treatment (CPB), the anaerobic sludge (A), the first aerobic sludge (O1), the second aerobic sludge (O2), the biological filter sludge (BF), the coagulation deposition sludge after biological treatment (CPA) and the discharge sludge (D), were collected. For the A/O/H/O plant, six sludge samples including the anaerobic sludge (A), the first aerobic sludge (O1), the hydrolysis sludge (H), the second aerobic sludge (O2), the coagulation deposition sludge after biological treatment (CPA) and the discharge sludge (D), were collected.

The sludge samples of 300 dm^3 in volume were freeze dried and placed in polyethylene bottles. The moisture contents of the sludge were 78.3–62.1%. Before speciation analysis, the sludge samples were grinded and sieved through a 200 mesh sieve (74 μm). The sieved sludge was further sampled by the method of coning and quartering to obtain homogeneous samples.

Modified BCR sequential extraction procedure. The homogeneous sludge samples were extracted by the modified BCR sequential extraction procedure [15] as follows.

Exchangeable metal fraction (F1): 0.5 g of dry sludge was placed in a 50 cm^3 polyethylene centrifugation tube, and 20 cm^3 of 0.11 mol·dm^{-3} acetic acid was added. The tube was shaken for 16 h at 25 °C at 120 rpm for extraction of heavy metals. After extraction, the centrifugation tube was centrifuged for 20 min at 4000 rpm. The supernatant liquid was collected in a 50 cm^3 volumetric flask and 5% nitric acid was added till the liquid level ran up to the constant volume line. The aqueous solution was passed through 0.45 μm filter membrane and then stored in polyethylene centrifugation tube before AAS analysis. The residue was washed with 10 cm^3 distilled water by shaking for 15 min at 4000 rpm.

Reducible metal fraction (F2): 20 cm^3 of 0.1 mol·dm^{-3} NH$_2$OH·HCl (pH 2 with HNO$_3$) was poured into the 50 cm^3 polyethylene centrifugation tube to extract heavy metals in the residue. The extraction was conducted for 16 h at 25 °C at 120 rpm. The other treatment steps were similar to those during extraction of the reducible metal fraction.

Oxidable metal fraction (F3): 5 cm^3 of 30% H$_2$O$_2$ was added into the residue at 25 °C. 1 h later, another 5 cm^3 of 30% H$_2$O$_2$ was added, and the polyethylene centrifugation tube was placed in a 85 °C water bath for digestion till the liquid died away. Then 25 cm^3 of 1 mol·dm^{-3} NH$_4$Ac (pH 2 with HNO$_3$) was added into the centrifugation tube

to extract the oxidable fraction. The tube was shaken at 120 rpm for 16 h at 25 °C. The other treatment steps were similar to those previously described.

Residual fraction (F4): The residue and 10 cm^3 of HNO$_3$, 10 cm^3 of HCl and 5 cm^3 of HClO$_4$ were placed in an Erlenmeyer flask which was then heated boiling using an electric jacket to nearly dry. Another 5 cm^3 of HNO$_3$, 5 cm^3 of HCl and 2.5 cm^3 of HClO$_4$ were added into the Erlenmeyer flask in turn, and the heated step was repeated. Then 5% of HNO$_3$ was used to dissolve the residue, and liquid phase was transferred into a volumetric flask. The residual fraction of Hg was extracted by the following steps: 2 cm^3 of mixture of H$_2$SO$_4$ and HNO$_3$ (v:v, 2:1) was added into the flask containing the residue, and 5 cm^3 of distilled water with 3 cm^3 of 5% KMnO$_4$ was added into the flask after violent reaction between the sludge and the mixed acid; the aqueous phase was heated to boiling for 5 min, and NH$_2$OH·HCl was added drop by drop until the purple solution turned into colorless.

The extraction procedure of total heavy metals was similar to that of the residual fraction.

Quality assurance. The standard material GBW08303 was applied for assessing the modified BCR sequential extraction procedure. The standard material was extracted just as the procedure of sludge sample. The content of exchangeable fraction, reducible fraction, oxidable fraction and residual fraction were marked as C_{F1}, C_{F2}, C_{F3} and C_{F4}, respectively. The sum of the content of the four fractions was marked as C_F, and the content of the total heavy metal was marked as C_T. The relative recoveries ($R1$, C_T/C_F) were between 83.9% and 106.8%. The recoveries ($R2$, $C_T/C_{standard}$) were 87.3–102.1% in comparison of the standard value ($C_{standard}$) of the standard material. All the results indicated that the modified BCR sequential extraction procedure was reliable.

3. RESULTS AND DISCUSSION

3.1. TOTAL CONTENTS OF HEAVY METALS

The total metals in the sludges were determined by the atomic absorption spectroscopy (AAS) employing the total heavy metal extraction process as a pretreatment procedure. The contents of Cd, Cr, Hg, Cu, Zn, Pb, Ni and As are shown in Tables 1 and 2. In the sludges from A/O/O, Zn was the most abundant heavy metal among the 8 ones (between 344 and 530 mg·kg^{-1}), and on the contrary the content of Hg was the lowest one in all sludges (between 3.34 and 13.8 mg·kg^{-1}). The contents of other heavy metals were between 5.0 and 119 mg·kg^{-1}. The total contents of heavy metals in sludges from A/O/H/O were between 4.87 and 788 mg·kg^{-1}. The most abundant one was Zn (between 449 and 788 mg·kg^{-1}) and Hg content was also the lowest one in all sludges (between

4.87 and 11.9 mg·kg^{-1}). The total heavy metal contents were similar as those reported by Alvarez et al. [23], however, the Hg content was higher. To sum up, the content of heavy metals in sludges from A/O/H/O was higher than that from A/O/O.

Table 1

Total content of heavy metals in sludge from A/O/O [mg·kg^{-1}]

Sludge	Cd	Cr	Hg	Cu	Zn	Pb	Ni	As
CPB	11.7	95.5	7.75	99	423	33.0	44.5	23.3
A	20.6	32.8	13.8	79.5	520.5	26.5	115	41.2
O1	12.0	33.8	8.00	120	411	40.1	95.5	24.1
O2	12.4	49.1	8.25	68.5	432	22.9	119	24.7
BF	15.5	41.4	10.3	75.5	530	25.2	113	30.9
CPA	5.00	26.5	3.34	96.5	344	32.2	38.8	10.0
D	6.87	65.2	4.58	111	425	37.1	76.4	13.7

Table 2

Total content of heavy metals in sludge from A/O/H/O [mg·kg^{-1}]

Sludge	Cd	Cr	Hg	Cu	Zn	Pb	Ni	As
A	9.36	68.3	7.20	674	652	241	83.0	21.3
O1	15.4	79.3	11.9	66.2	788	23.7	274	35.1
H	13.7	70.9	10.5	590	700	211	128	31.1
O2	13.5	79.3	10.4	319	723	114	184	30.8
CPA	6.33	86.7	4.87	138	449	49.3	88.3	14.4
D	8.15	70.9	6.27	141	612	50.2	89.3	18.5

3.2. FRACTIONS OF HEAVY METALS IN VARIOUS SLUDGES

All sludges were subjected to extraction by the four step modified BCR sequential extraction procedure. Percentage distribution of heavy metals in fractions of sludge A/O/O (F1– exchangeable, F2 – reducible, F3 – oxidable, F4 – residual) is shown in Figs. 1, 2, and that for A/O/H/O in Figs. 3, 4.

In sludges from A/O/O, the residual speciation was the predominant speciation except O unit. For the 8 heavy metals, the numbers of predominant residual speciation for A, CPB, O2, BF, CPA and D sludge were 8, 4, 3, 6, 5 and 5, respectively. For the CPB sludge, the residual speciation of Cu, Zn, Pb and Ni was the predominant speciation, especially up to 90.4% for Cu. The oxidable fraction was higher than that of Cd, Hg and As which was above 50%. The residual fraction of Zn, which still reached 44.3%, was the lowest one among the 8 heavy metals.
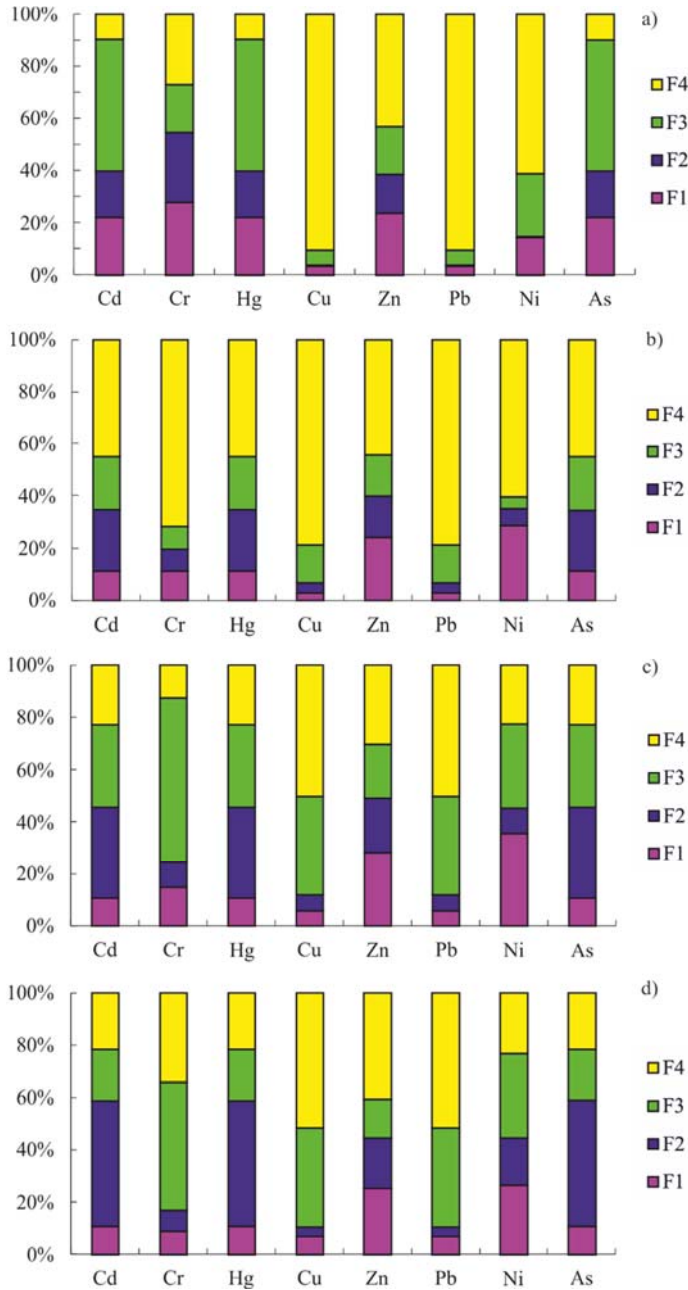
Fig. 1. Percentage distribution of heavy metals in fractions of sludge for the A/O/O:
a) sludge before biological treatment (CPB), b) anaerobic sludge (A), c) the first aerobic sludge (O1),
d) the second aerobic sludge (O2); F1 – exchangeable metal fraction,
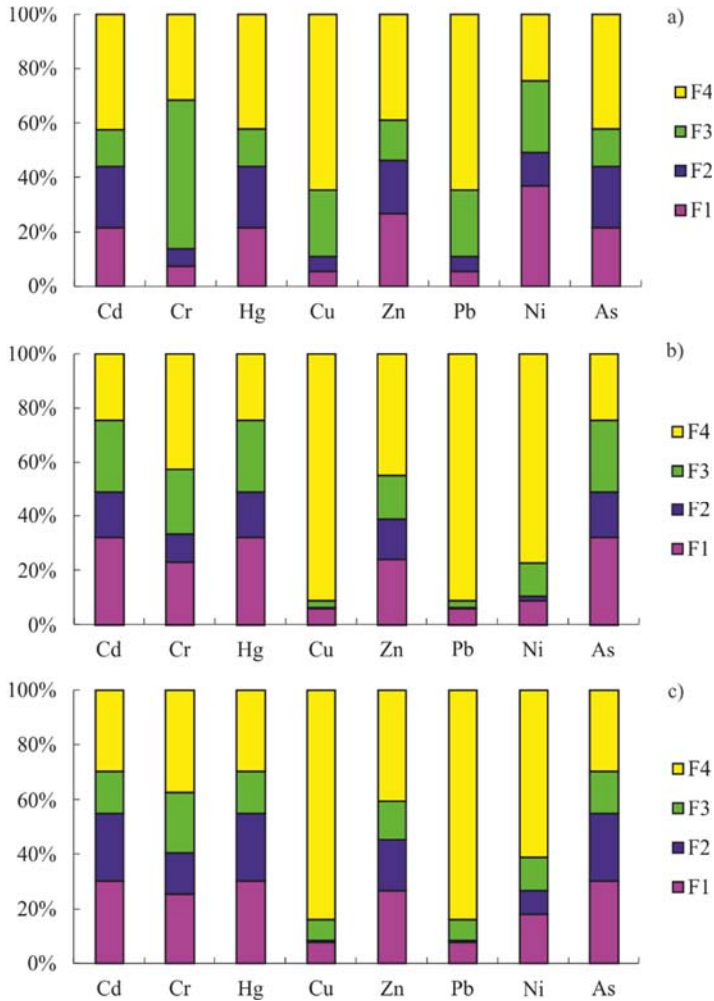F2 – reducible metal fraction, F3 – oxidable metal fraction, F4 – residual fraction)

Fig. 2. Percentage distribution of heavy metals in fractions of sludge for the A/O/O:
a) biological filter sludge (BF), b) coagulation deposition sludge after biological treatment (CPA),
c) discharge sludge (D); F1 – exchangeable metal fraction, F2 – reducible metal fraction,
F3 – oxidable metal fraction, F4 – residual fraction)

Greater oxidable fraction was found in the sludge from O1 unit compared to that from A unit, and simultaneously no significant differences were found for the exchangeable and reducible fraction. The differences in the the oxidable fractions may be explained taking into account that heavy metals changed their forms after aerobic condition treatment, hence the heavy metals were easier extracted by NH_4Ac after oxidization by H_2O_2. It rarely occurred that the exchangeable fraction of Ni was the predominant fraction among 8 heavy metals in all sludges which was up to 30.6%.
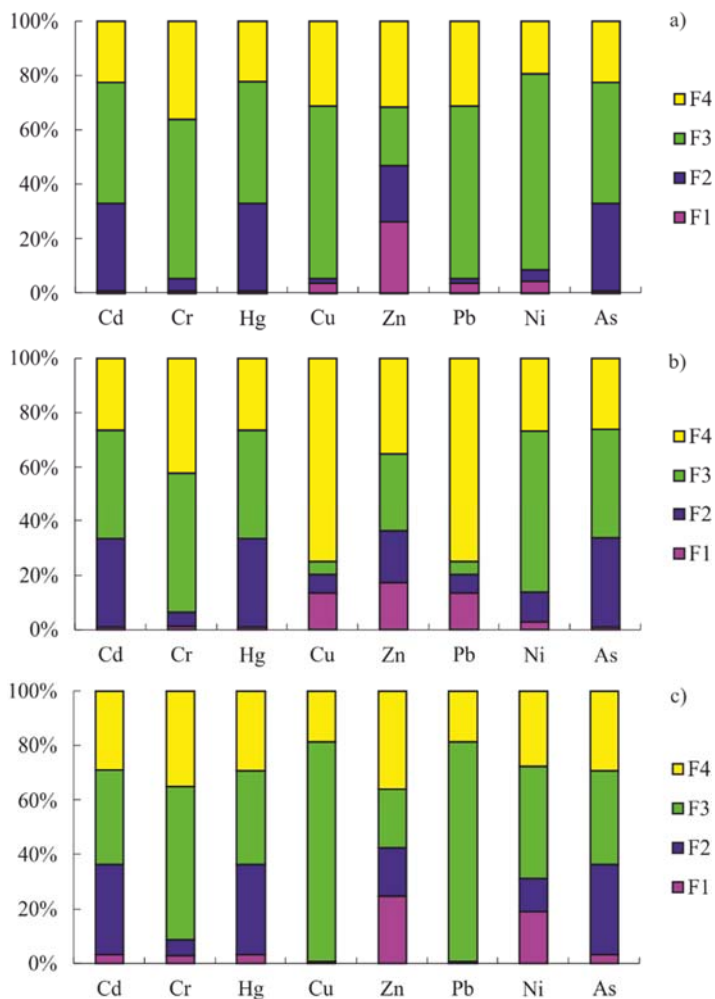
Fig. 3. Percentage distribution of heavy metals in fractions of sludge for the A/O/H/O:
a) anaerobic sludge (A), b) the first aerobic sludge (O1), c) the hydrolysis sludge (H);)
F1 – exchangeable metal fraction; F2 – reducible metal fraction;
F3 – oxidable metal fraction; F4 – residual fraction)

In comparison to the sludge from the O1 unit, higher reducible fraction, especially for Cd, Hg and As, occurred in the sludge from the O2 unit which may stem from the stronger oxidization rooted in higher oxygen concentration in O2 unit to remove the NH_4^+-N contaminant in coking wastewater. As to the BF sludge, the residual speciation was also the predominant fraction, and it was worthwhile to note that the exchangeable fraction of Ni was the highest speciation. Compared with the sludges from biological units, higher exchangeable fractions were found in the sludge from CPA unit which could be interpreted that the different sludges led to different interactions between heavy metals and the sludge.
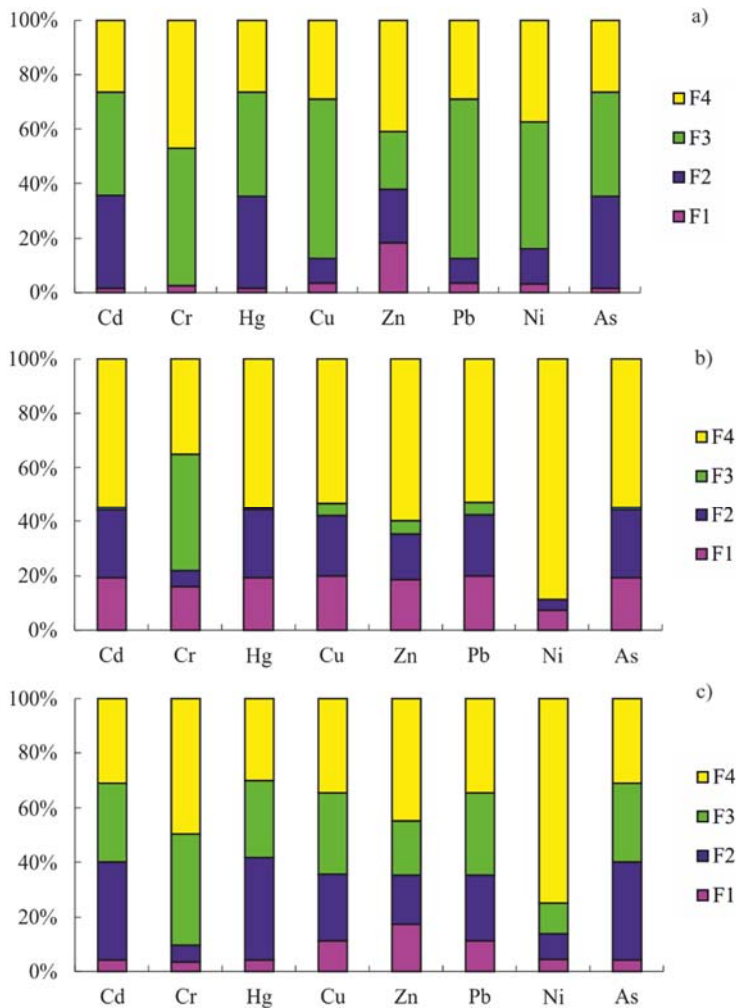
Fig. 4. Percentage distribution of heavy metals in fractions of sludge for the A/O/H/O:
a) the second aerobic sludge (O2), b) coagulation deposition sludge after biological treatment (CPA),
c) discharge sludge (D); F1 – exchangeable metal fraction, F2 – reducible metal fraction,
F3 – oxidable metal fraction, F4 – residual fraction)

Heavy metals were mainly trapped by the agglomeration by means of adsorption in the CPA unit. As regards the biological unit sludge, heavy metals may pass into the cell after adsorbing by the microorganisms and turned into one part of the microorganisms, therefore, the heavy metals were more difficult to be extracted by acetic acid. The exchangeable fractions of Cd, Hg and As were all higher than 30%, the exchangeable fractions of Cr and Zn were the second high speciation which reached 22.9 and 24.1%, respectively. The fractions of heavy metals in the discharged sludge were very similar

to those from the sludge from the CPA unit as that the CPA sludge was the main source of the discharged sludge for A/O/O.

The most obvious characteristic of the fractions of the heavy metals in the sludges from the A/O/H/O plant was that at least one speciation of every heavy metal might be disregarded, and correspondingly that the oxidable fractions increased to a great extent compared with those of A/O/O. The most common fraction which could be disregarded was the exchangeable fraction. In the sludge from A unit, the exchangeable fraction for Cd, Hg and As could be disregarded, and the fraction of 7 in total 8 heavy metals was the predominant speciation with up to 72.4% for Ni as the highest one. The residual fraction of the heavy metals in O1 sludge increased in contrast with that of A unit especially for Cu and Pb with the residual fraction up to 74.7% and 73.5%, respectively. The fraction characteristic of the heavy metals in the H sludge was very similar to that of A sludge probably due to the similar treatment conditions between the two units. The fractions of heavy metals in CPA sludge were also the predominant speciation with 7 in 8 heavy metals as the primary speciation. Just like the CPA sludge of A/O/O due to the same reason, the exchangeable fraction was higher than that of the other unit sludges of A/O/H/O. The D sludge was the complex of the five former sludges, and the fraction characteristic and emission quantity decided on the fraction characteristic of heavy metals in D sludge. The clear differences between the CPA and D sludges made clear that the CPA sludge was not the main source of the D sludge which was distinct with that of A/O/O. The results were in accordance with most sludge that the oxidable and residual fraction were the dominant speciation [18, 19].

3.3. FRACTIONS OF DIFFERENT SPECIATIONS FOR HEAVY METALS

The exchangeable fraction was mobile and available for living beings, and the reducible fraction was also the biological availability speciation. The total content of the exchangeable and the reducible speciation determined the toxicity of the heavy metals in sludges. It is difficult for living beings to make use of the oxidable and the residual fraction, hence that the content of the oxidable and residual speciation takes minor contribution to the toxicity of heavy metals. In order to present the potential environment risk of the produced sludge during the treatment of coking wastewater, the fractions of selected heavy metals based on different speciation have been examined.

A fraction of heavy metals based on different speciation in sludges from A/O/O is shown in Fig. 5. The exchangeable fraction of Cu and Pb in all sludges was even lower than 10%, exhibiting very poor biological availability. The Ni exchangeable fraction in biological units was the highest one with the value of nearly 40%. The Zn exchangeable fraction ranging from 23.5 to 28.3% was slightly affected by the unit conditions. With regards to the reducible fraction, Cu and Pb contents were similar to those of exchangeable fraction.
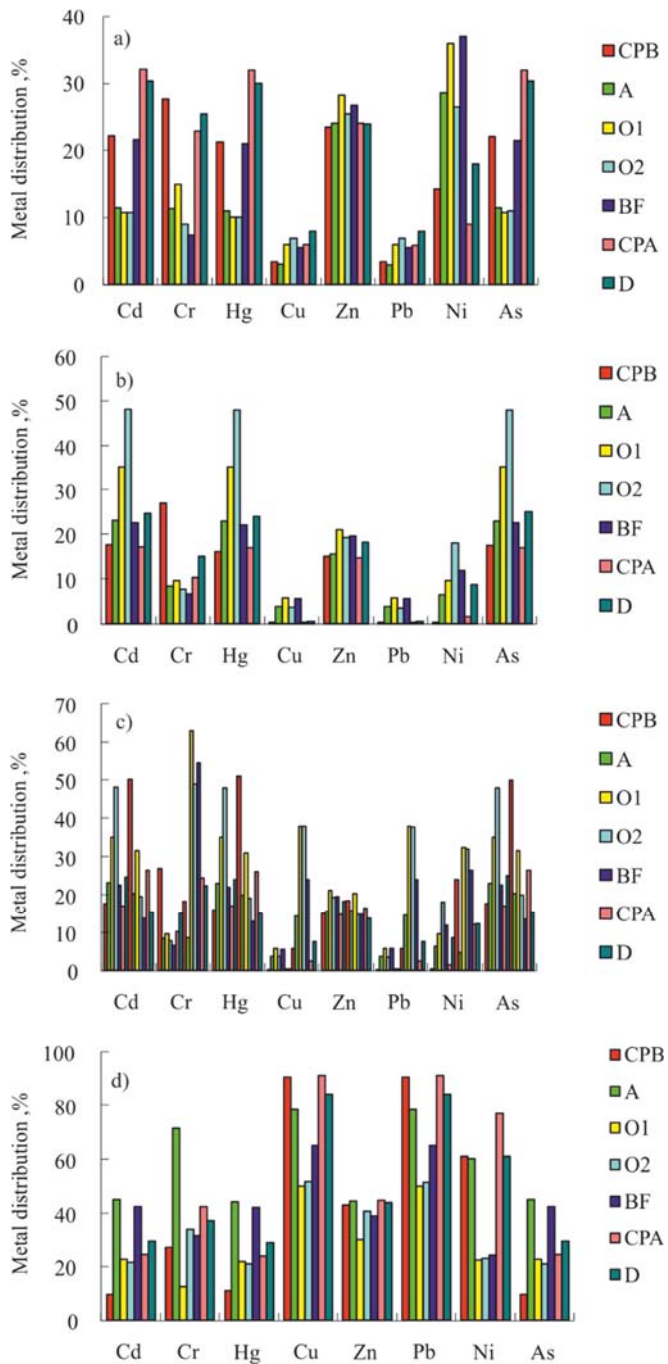
Fig. 5. Fractions of the selected heavy metals based on different speciation for the A/O/O process:
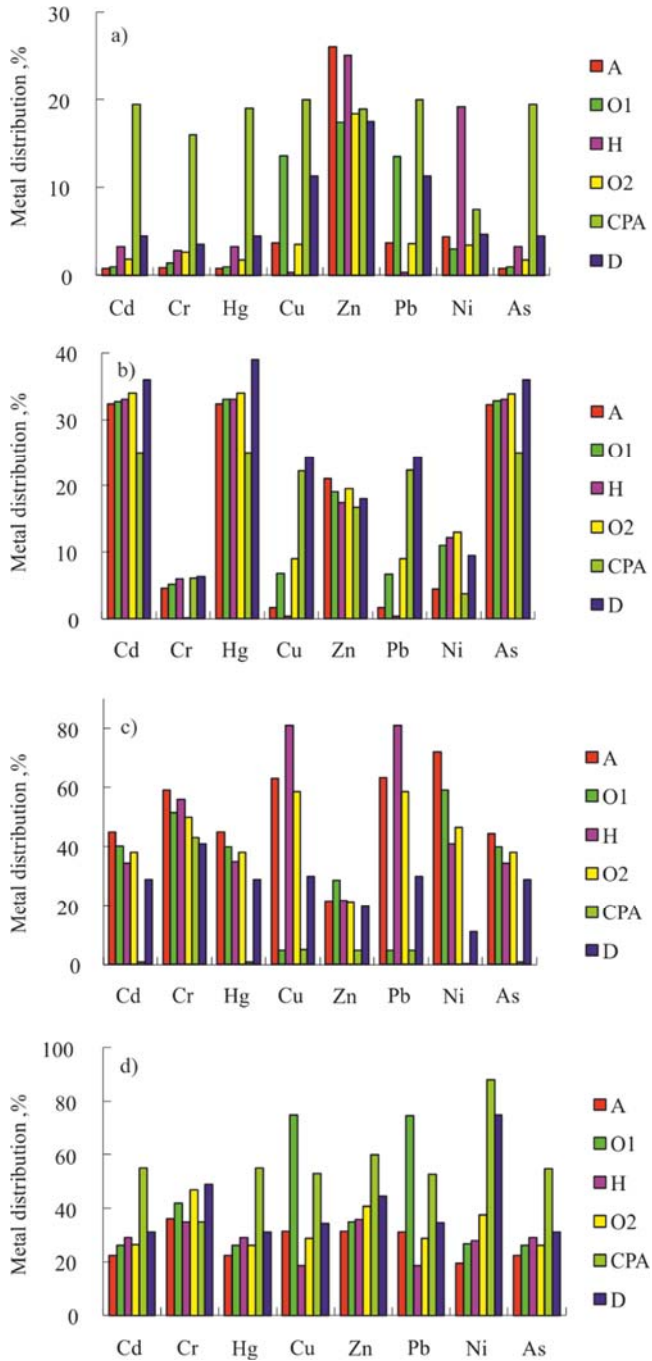a) exchangeable fraction, b) reducible fraction, c) oxidable fraction, d) residual fraction)

Fig. 6. Fractions of the selected heavy metals based on different speciation for the A/O/H/O process:
a) exchangeable fraction, b) reducible fraction, c) oxidable fraction, d) residual fraction)

The fraction of Cd, Hg and As was the most significant high speciation with the higher value up to nearly 50% of biological units. Zn reducible fraction was also affected by unit conditions with the slightly lower value than that of the exchangeable fraction. The oxidable fraction of Cr was the highest speciation among the 8 heavy metals, especially that the value of O1 unit was high, up to 62.8%. The obvious characteristic of the reducible fraction was that the higher fraction was found in biological units. The residual fraction was the predominant speciation in most sludges for heavy metals. More than half of the fractions were above the value of 40%.

In comparison of the exchangeable fraction of A/O/O, the exchangeable fraction of heavy metals in sludges from A/O/H/O was much lower except for Zn with slight decreases. The result made further proof that the unit conditions caused little effect on the fraction of Zn. Enormous variations were found among different sludges for the exchangeable fraction. By comparison the values of the reducible fractions of heavy metals in sludges from A/O/H/O were higher than that of A/O/O, and whatever the reducible fractions of Cr, Hg and As were the highest speciation as that of A/O/O. Slight differences of the oxidable and residual fraction in comparison of A/O/O with a little higher oxidable fraction and a little lower residual fraction. In A/O/H/O sludges, the total values of heavy metals fractions from high to low were in the order of the residual, oxidable, reducible and exchangeable fraction.

3.4. CLUSTER ANALYSIS

It is difficult to draw general conclusions on the fractions of heavy metals in sludges due to substantial variations in the fraction values. In this work, the SPSS software was employed to interpret the general regularities in the fractions of the heavy metals in sludges. Cluster analysis was conducted based on the fraction values.
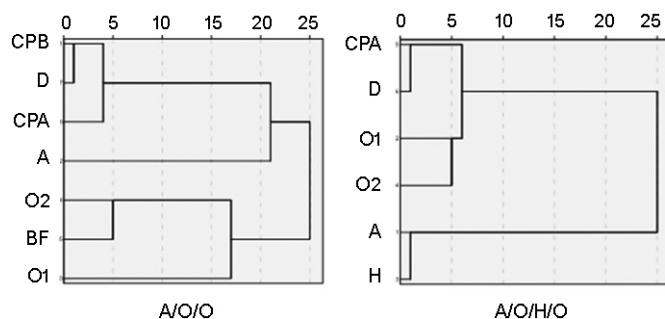

Fig. 7. Cluster analysis of heavy metals
based on various units for the A/O/O process

Figure 7 shows the results of cluster analysis based on different units. In the figure, short distance indicated close relationship of heavy metals, and that of the opposite. It is clear that the units with similar conditions could be classified into one category. With

the A/O/H/O, for example, the fractions of heavy metals in sludges from A and H units, O1 and O2 units with similar treatment conditions could be classified into one basic category, respectively. It was similar for the A/O/O plant. This demonstrated that the treatment condition was one key factor affecting the fractions of heavy metals in sludges from coking wastewater treatment plants.
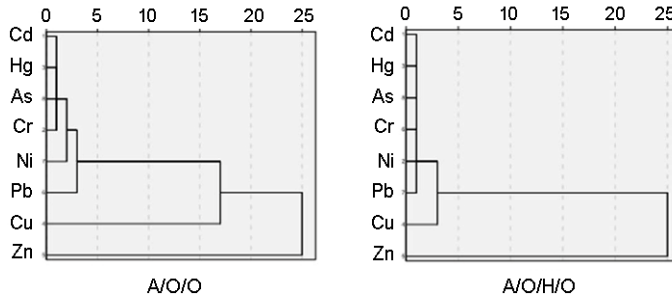

Fig. 8. Cluster analysis of heavy metals
based on different units for the A/O/H/O process

Figure 8 shows the cluster analysis result based on various heavy metals. Cd, Hg, As and Cr were classified together in sludges not only from A/O/O but from A/O/H/O. Cu and Zn were the two heavy metals far away from this basic category. The outcome turned up that the intrinsic characteristic of heavy metals was another key factor affecting on the fractions of heavy metals.

4. CONCLUSIONS

The exchangeable, reducible, oxidable and residual fractions of Cd, Cr, Hg, Cu, Zn, Pb, Ni and As in sludges from two typical treatment plants were examined by the modified BCR sequential extraction procedure. The total content of the 8 heavy metals in sludges from coking wastewater treatment plants varied from 3.34 to 788 mg·kg^{-1} with Hg as the lowest and Zn as the highest one which content were 3.34–13.8 and 344–788 mg·kg^{-1}, respectively. The residual fraction was the predominant speciation followed by the oxidable fraction. Poor biological availability of heavy metals was found in sludges from typical coking wastewater treatment plants. The cluster analysis of the fractions conducted by SPSS revealed that the treatment condition and the intrinsic characteristic of heavy metals were the two key factors determining the fractions.

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