

## Screening long-time plating effluent qualities by sorbent sorption with XRF analysis

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### Abstract

Long-term monitoring of plating effluent quality traditionally requires dense frequency sampling and analysis for multiple elements are needed. An effective and rapid approach was developed to monitor long-time plating effluent quality. The approach employs the placement of low-cost sorbents (chitosan, zeolite and granular activated carbon) in plating effluents followed by analysis of multiple-element X-ray fluorescence (XRF). Three plating effluents were selected in this study. Laboratory Freundlich isotherm sorption experiments were also conducted to describe the relationships of metal concentrations on sorbents and in effluents. Results indicated that chitosan was a suitable sorbent to estimate the Zn, Ni and Cr concentrations in plating effluents. Granular activated carbon was suitable for Cu concentration monitoring in effluents. The accumulation of metals onto sorbents with different sorption periods (1–3 days) was also investigated.

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**Keywords:** Long-term monitoring; Effluent quality; Sorption; Chitosan; XRF

### 1. Introduction

Improperly treated and untreated plating effluents containing high concentrations of heavy metals pose a great risk for environmental and human health. The metal concentrations in real effluents may fluctuate with time. Thus, close monitoring through high-density effluent sampling is necessary. However, developing countries often have numerous small geographically dispersed plating factories. Close monitoring in these cases becomes difficult because of high time- and labor-cost.

Many low-cost sorbents, such as chitosan and zeolite, have been investigated for metal removal in wastewater, because of

their excellent metal sorption capacities as compared to activated carbon [1,2]. Chitosan is derived by alkaline *N*-deacetylation of chitin that widely exists in the exoskeleton of shellfish and crustaceans. Its amine groups can effectively bind with heavy metals [3]. The three-dimensional structure of zeolite consists of SiO<sub>4</sub> and AlO<sub>4</sub> tetrahedral providing negatively charged sites for ion exchange [2]. However, besides the nature of sorbents, operating conditions influence their sorption capacity, such as metal concentrations, solution pH, chelating agents and contact time [2,4,5].

X-ray fluorescence (XRF) is a well-established technique for non-destructive analysis of metals in different materials. It has the advantages of speed, convenience, multi-element analysis, precision and accuracy and minimal sample treatment [6]. The X-rays generated from a radioactive source excite the elements in the sample which then emit fluorescence. Each element has a unique set of emitted energy. An XRF analyzer can deduce the identity and quantities of the elements in samples. It is very suitable for rapid determination of multi-metal concentrations on site. The detection limits of portable XRF for Pb, Cd, Zn and Cu are low (20–60 mg/kg), as opposed to those of Ni (150 mg/kg)

**Abbreviations:**  $C_{\text{estimated}}$ , the estimated metal concentrations based on Freundlich sorption constants ( $\text{mg l}^{-1}$ );  $C_{\text{before}}$ , metal concentration in effluent before sorbent sorption in effluent ( $\text{mg l}^{-1}$ );  $C_{\text{after}}$ , metal concentration in effluent after sorbent sorption in effluent ( $\text{mg l}^{-1}$ );  $S_{\text{metal}}$ , metal concentration sorbed onto sorbent ( $\text{mg kg}^{-1}$ )

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and Cr (300 mg/kg) [7]. Pb and Cd have not been studied in this work and therefore their detection limits are not relevant in this paper.

Monitoring plating effluent qualities is very important for environmental protection. To our knowledge, there is no related study applying sorbents to screen day-based plating effluent qualities. In this study, a simple approach combining low-cost sorbents and XRF measurement was developed to monitor a day-based plating effluent quality. Isothermal sorption experiments were conducted to estimate the possible minimum metal concentrations of effluents. The factors influencing metal sorption on sorbents were also investigated. The objectives of this study were:

- (1) To compare the suitability of three sorbents used for metal sorption in effluents.
- (2) To use the Freundlich equation to describe the relationship of metal concentrations between sorbents and effluents.

The above information was used to develop an effective to monitor long-time plating effluent quality.

## 2. Materials and methods

### 2.1. Sampling sites and scheme

Three different plating effluents (assigned as effluents 1, 2 and 3) were selected. The sampling period was from November 22 to 23, 2004. The sampling scheme for effluents and sorbents are described in Table 1. Three sorbents, chitosan flake (Kiotek Corp., Taiwan), zeolite (Hayashi Pure Chemical Ind. Japan) and commercial granular activated carbon were used as received. A 15 g sorbent was put in plastic net bags and placed in the center of effluents for different sorption periods (1–3 days) (Fig. 1). At a pre-set time, the sorbent was removed, washed with distilled water, air-dried and placed in an oven (40 °C) for 24 h. Effluent samples before and after the sorbent sorption period in the effluents were taken and preserved at 4 °C until analysis.

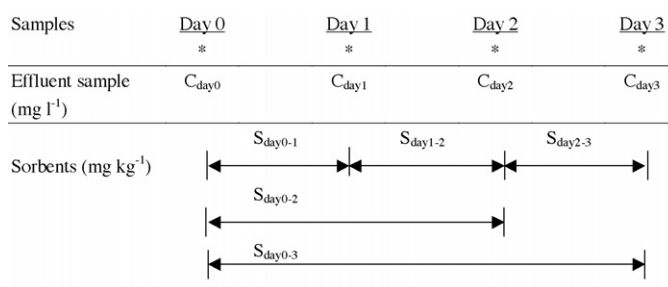


Fig. 1. Sampling scheme for effluents sample and sorbent sorption.

### 2.2. Measurement of metal concentrations in effluent and sorbent

The metal concentrations of effluents were analyzed by ICP-AEC (EPA 601 0B) or flame atomic absorbance spectrophotometry (NIEA W306.52A, Taiwan). COD was determined by closed reflux method (NIEA W517.50B, Taiwan). The metal concentrations on sorbents were analyzed with a portable XRF (Niton XL-700S, Cadmium 109 and Am 241 sources, L X-ray, SI PIN-diode detector) according to USEPA Method 6200. A 10 g sorbent was used for analysis and the detection time was 10 min for each Cadmium 109 and Am 241 source. The quality control procedure was conducted according to NIST certified soil samples with high, medium and low standards. Calibration check, method blank and precision test were conducted daily as quality control measures before XRF analysis. The quality control standards are calibration check: the percent difference (%D) is less than 20%; R.S.D. of duplicate is less than 30% for seven replicate measurements.

### 2.3. Laboratory sorption experiments

For sorption experiment, 0.2 g sorbent (either chitosan or activated carbon) was added to 300 ml flask containing 200 ml metal solution at the concentrations of 0, 6.25, 12.5, 25 and 10 mg l<sup>-1</sup>. The solution was adjusted to the desired pH with 0.1 M NaOH and 0.1 M HCl. The flask was sealed with parafilm and shaken in a water bath (20 °C, 50 rpm) for 24 h according to the sorption

Table 1  
Effluent characteristics of plating factories (metal concentration unit: mg l<sup>-1</sup>)

| Effluent | Time  | pH  | COD | Cu    | Ni    | Zn     | Cr     | Pb    | Cd |
|----------|-------|-----|-----|-------|-------|--------|--------|-------|----|
| 1        | Day 0 | 6.3 | 284 | 0.038 | 0.495 | 0.205  | 0.003  | 0.000 | ND |
|          | Day 1 | 6.3 | 133 | 0.029 | 1.135 | 0.077  | 0.006  | ND    | ND |
|          | Day 2 | 6.4 | 67  | 0.034 | 0.181 | 0.017  | 0.010  | ND    | ND |
|          | Day 3 | 7.2 | 127 | 0.041 | 3.657 | 0.026  | 0.051  | 0.003 | ND |
| 2        | Day 0 | 3.6 | 68  | 4.590 | 1.254 | 48.718 | 2.654  | 0.032 | ND |
|          | Day 1 | 5.0 | 9   | 5.638 | 1.990 | 3.508  | 20.970 | 0.002 | ND |
|          | Day 2 | 3.8 | 27  | 5.741 | 4.625 | 21.471 | 7.461  | 0.013 | ND |
|          | Day 3 | 6.6 | 23  | 0.208 | 4.647 | 8.859  | 0.953  | 0.003 | ND |
| 3        | Day 0 | 7.7 | 6   | 0.136 | 0.156 | 0.026  | 0.305  | 0.000 | ND |
|          | Day 1 | 8.1 | 19  | 0.410 | 0.311 | 0.016  | 0.212  | 0.003 | ND |
|          | Day 2 | 6.5 | 3   | 0.002 | 0.082 | 0.005  | 0.011  | 0.002 | ND |
|          | Day 3 | 6.7 | 17  | 0.002 | 0.035 | 0.012  | 0.076  | ND    | ND |

ND: below detection limits.

period in effluents. At pre-set time intervals, 3 ml samples were taken, filtered by Whatman 42 and analyzed by AAS. Duplicate experiments were conducted.

The amount of sorption at equilibrium,  $q_e$  ( $\text{g mg}^{-1}$ ), was calculated by:

$$q_e = \frac{(C_0 - C_e)V}{W}$$

where  $C_0$  and  $C_e$  are the initial and 24 h sorption-period metal concentrations, respectively.  $V$  and  $W$  are the solution volume (l) and the weight of chitosan used (g), respectively. The Freundlich equation was used to describe the metal sorption behavior onto sorbent.

$$q_e = K_F C_e^{1/n} \quad (1)$$

where  $K_F$  ( $\text{mg g}^{-1}$ ) and  $1/n$  are Freundlich constant and exponent, respectively. A linear form of the Freundlich equation will generate the constants  $1/n$  and  $K_F$ .

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_F$$

The isotherm parameters of the Freundlich model obtained from sorption experiments in the laboratory were used to estimate the metal concentrations in effluents.

### 3. Results and discussion

#### 3.1. Effluent properties and metal concentrations on sorbents

The pH, COD and metal concentrations of three effluents on different sampling days are listed in Table 1. The metal concentrations presented here are the effluent samples taken before ( $C_{\text{before}}$ ) and after ( $C_{\text{after}}$ ) sorbent sorption in the effluents. Table 1 shows that the metal concentrations in effluents might change temporally. The pH of effluent 1 was neutral (6.3–7.2). It contained higher organic matter ( $\text{COD} = 67\text{--}284 \text{ mg l}^{-1}$ ) than effluent 2 and effluent 3 ( $\text{COD} = 3\text{--}68 \text{ mg l}^{-1}$ ). Ni was the predominant metal (0.18–3.65  $\text{mg l}^{-1}$ ) and trace metals (Cu, Zn and

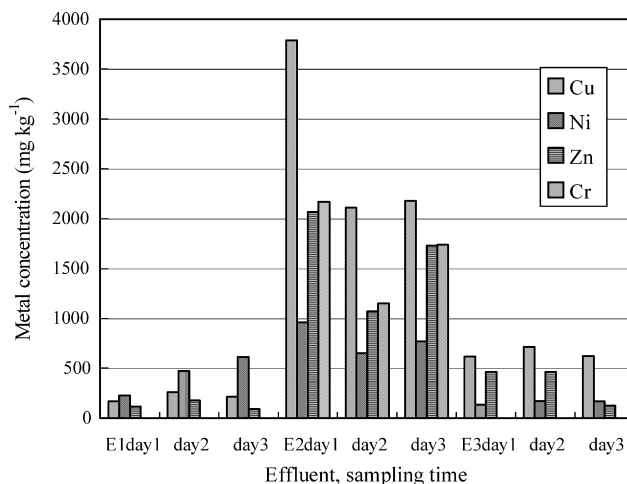


Fig. 3. Sorbed metal concentrations onto chitosan. Sorption period was one day.

Cr) were also detected ( $<0.2 \text{ mg l}^{-1}$ ) in effluent 1. Effluent 2 contained high concentrations of Cu, Ni, Zn and Cr. This implies that the effluent was not well treated before discharge. The order of metal concentrations in effluent 2 was  $\text{Zn} > \text{Cr} > \text{Cu} \approx \text{Ni}$ . Its pH values ranged from acidic (pH 3.6) to neutral (pH 6.6). The concentrations of Cu, Ni and Cr in effluent 3 were lower ( $<0.41 \text{ mg l}^{-1}$ ).

The daily metal concentrations ( $S_{\text{day}0-1}$ ,  $S_{\text{day}1-2}$  and  $S_{\text{day}2-3}$ ) of sorbents analyzed by XRF are shown in Figs. 2–4. The measured metal concentrations of sorbents are not considered in this study if they are below the detection limits of XRF and the background levels of sorbents (Table 2).

When comparing results of metal concentrations in effluents (Table 1) and in zeolite, zeolite effectively sorbed Cu and Cr but not Ni (Fig. 2). Fig. 3 indicates that chitosan posed excellent sorption capacities especially for Cu and also for Ni, Zn and Cr. For example, of the metal concentrations in effluents, copper was not the highest. However, the corresponding copper concentration of chitosan was the highest. Comparisons of the metal concentrations of these three sorbents (Figs. 2–4) show

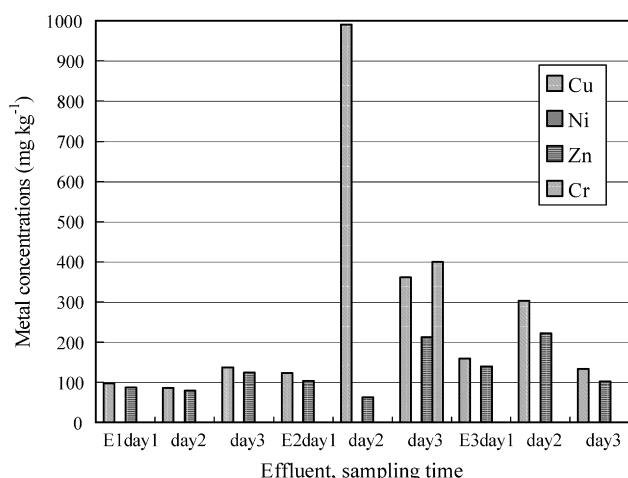


Fig. 2. Sorbed metal concentrations onto zeolite. Sorption period was one day.

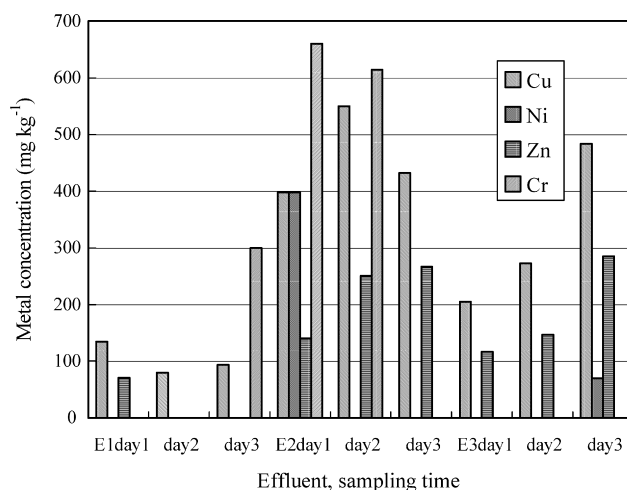


Fig. 4. Sorbed metal concentrations onto granular activated carbon. Sorption period was one day.

Table 2  
XRF detection limits and metal background levels of sorbents (unit: mg kg<sup>-1</sup>)

| Metal                            | Cu  | Ni  | Zn | Cr  | Pb | Cd |
|----------------------------------|-----|-----|----|-----|----|----|
| XRF detection limit <sup>a</sup> | 60  | 150 | 50 | 300 | 20 | 35 |
| Background level                 |     |     |    |     |    |    |
| Zeolite                          | ND  | ND  | ND | ND  | ND | ND |
| Chitosan                         | 196 | ND  | 97 | 101 | ND | ND |
| GAC                              | 152 | ND  | 69 | 180 | ND | ND |

<sup>a</sup> Niton XL-700S manual.

that chitosan had much higher metal sorption capacities than zeolite and GAC. Comparison of metal concentrations in effluents (Table 1) and onto GAC (Fig. 4) indicated that GAC was effective in sorption of Cr and Cu.

The metal concentrations in effluent changed temporally (Table 1). Thus, the  $C_{\text{before}}$  and  $C_{\text{after}}$  could not represent the real long-time metal concentration in effluents. The possible minimum daily metal concentrations in effluents were estimated based on sorbed metal concentrations on sorbents. Because chitosan has excellent sorption ability on Cu, Ni, Zn and Cr, it was selected in following research.

### 3.2. Estimate metal concentrations in effluents by Freundlich model

To estimate the possible daily metal concentrations in effluents based on sorbed metal concentrations on chitosan, the laboratory sorption experiments were conducted at different pH values (4–7) to obtain the isotherm constants. Generally, the equilibrium times for Ni, Zn and Cr were shorter than 3 h, while the sorption equilibrium time for copper was longer than 48 h (data not shown). A 24-h sorption period was selected in this laboratory study, according to the chitosan sorption in three effluents. The Freundlich isotherm equation was employed to describe the relationship of metal concentrations onto chitosan and in solution.

Table 3 indicates that the Freundlich models described the relationship of concentrations for sorption of Ni, Zn, Cr and Cu onto chitosan and in solution well at pH 4–7, except for Cu at pH above 5 and Cr at pH 7. The Freundlich equations obtained from laboratory sorption experiments were then used to

Table 3  
Freundlich sorption constants for Ni, Zn, Cr and Cu sorption onto chitosan

| pH 4 | 1/n   | $K_F$ | $r^2$ | pH 5 | 1/n   | $K_F$ | $r^2$ |
|------|-------|-------|-------|------|-------|-------|-------|
| Ni   | 0.589 | 0.146 | 0.987 | Ni   | 0.635 | 0.660 | 0.960 |
| Zn   | 1.622 | 0.023 | 0.955 | Zn   | 0.495 | 1.341 | 0.970 |
| Cr   | 1.506 | 0.059 | 0.985 | Cr   | 2.203 | 0.095 | 0.974 |
| Cu   | 0.336 | 6.410 | 0.978 | Cu   | 0.410 | 0.304 | 0.828 |
| pH 6 | 1/n   | $K_F$ | $r^2$ | pH 7 | 1/n   | $K_F$ | $r^2$ |
| Ni   | 0.754 | 0.242 | 0.916 | Ni   | 0.289 | 0.701 | 0.994 |
| Zn   | 0.643 | 0.617 | 0.984 | Zn   | 0.560 | 1.067 | 0.970 |
| Cr   | 0.621 | 0.672 | 0.998 | Cr   | 1.952 | 0.024 | 0.896 |
| Cu   | 0.258 | 10.1  | 0.881 | Cu   | –     | –     | –     |

Sorption period was 24 h.

estimate the possible long-time metal concentrations ( $C_{\text{estimated}}$ ) in effluents based on the corresponding metal concentrations sorbed onto sorbents ( $S_{\text{metal}}$ ). The isotherm constants selected for calculating  $C_{\text{estimated}}$  were based on the effluent pH after the sorbent sorption period.  $C_{\text{estimated}}$  was compared with the metal concentrations in effluent samples before ( $C_{\text{before}}$ ) and after ( $C_{\text{after}}$ ) the chitosan sorption period in effluents to evaluate whether high metal concentration effluents occurred during the sorbent sorption periods.

Table 4 shows the  $C_{\text{estimated}}$ ,  $C_{\text{before}}$  and  $C_{\text{after}}$  of Ni, Zn and Cr in three effluents. The  $C_{\text{estimated}}$  was not calculated where sorbed metal concentrations on the sorbents were smaller than the background concentrations of sorbents (Table 2). Generally, the  $C_{\text{estimated}}$  of Ni, which was calculated from the isotherm constants obtained from the laboratory chitosan sorption experiment, was close to the corresponding  $C_{\text{before}}$  and  $C_{\text{after}}$ , except for effluent with high pH (effluent 1, day 1). It is interesting that the  $C_{\text{estimated}}$  of Ni in effluent 1 day 2 was higher than the corresponding  $C_{\text{before}}$  and  $C_{\text{after}}$ . The  $C_{\text{before}}$  and  $C_{\text{after}}$  do not represent the long-time metal concentrations in effluents, because the real metal concentrations in plating effluents often fluctuate. This approach developed in this study can effectively estimate the possible high metal concentrations in the plating effluent. Although the real metal concentrations in effluents can be comprehended by dense sampling, it becomes infeasible due to the fact that plating factories are numerous.

Table 4  
The estimated concentrations of Ni, Zn and Cr from chitosan sorption isotherm and measured concentrations from effluents

| Effluent | pH    | Ni                     |                     |                    | Zn                     |                     |                    | Cr                     |                     |                    |       |
|----------|-------|------------------------|---------------------|--------------------|------------------------|---------------------|--------------------|------------------------|---------------------|--------------------|-------|
|          |       | $C_{\text{estimated}}$ | $E_{\text{before}}$ | $E_{\text{after}}$ | $C_{\text{estimated}}$ | $E_{\text{before}}$ | $E_{\text{after}}$ | $C_{\text{estimated}}$ | $E_{\text{before}}$ | $E_{\text{after}}$ |       |
| 1        | Day 1 | 6.3                    | 0.91                | 0.50               | 1.14                   | –                   | 0.21               | 0.08                   | –                   | 0.003              | 0.006 |
|          | Day 2 | 6.4                    | 2.43                | 1.14               | 0.18                   | –                   | 0.08               | 0.02                   | –                   | 0.006              | 0.01  |
|          | Day 3 | 7.2                    | 0.63                | 0.18               | 3.66                   | –                   | 0.02               | 0.03                   | –                   | 0.01               | 0.05  |
| 2        | Day 1 | 5                      | 1.81                | 1.25               | 1.99                   | 2.40                | 48.72              | 3.51                   | 4.13                | 2.65               | 20.97 |
|          | Day 2 | 3.8                    | 12.52               | 1.99               | 4.63                   | 10.67               | 3.51               | 21.47                  | 7.15                | 20.97              | 7.46  |
|          | Day 3 | 6.6                    | 4.64                | 4.63               | 4.65                   | 9.66                | 21.47              | 8.86                   | 4.63                | 7.46               | 0.95  |
| 3        | Day 1 | 8.1                    | –                   | 0.16               | 0.31                   | –                   | 0.03               | 0.02                   | –                   | 0.31               | 0.21  |
|          | Day 2 | 6.5                    | –                   | 0.31               | 0.08                   | 0.64                | 0.02               | 0.01                   | –                   | 0.21               | 0.01  |
|          | Day 3 | 6.7                    | –                   | 0.08               | 0.04                   | 0.05                | 0.01               | 0.01                   | –                   | 0.01               | 0.08  |

(–) Not estimated because of the metal background concentrations of chitosan.

Table 5

The estimated concentrations of Cu from chitosan and GAC sorption isotherm and measured concentrations from effluents

| Effluent |       | pH  | $C_{\text{estimated}}$<br>(based on<br>chitosan) | $C_{\text{estimated}}$<br>(based on<br>GAC) | $C_{\text{before}}$ | $C_{\text{after}}$ |
|----------|-------|-----|--|---|---------------------|--------------------|
| 1        | Day 1 | 6.3 | $1.3 \times 10^{-7}$                             | 0.04  | 0.04                | 0.03               |
|          | Day 2 | 6.4 | $7.1 \times 10^{-7}$                             | 0.01  | 0.03                | 0.03               |
|          | Day 3 | 7.2 | –  | –   | 0.03                | 0.04               |
| 2        | Day 1 | 5.0 | $4.7 \times 10^2$                                | 4.10  | 4.59                | 5.64               |
|          | Day 2 | 3.8 | $3.7 \times 10^{-2}$                             | 8.49  | 5.64                | 5.74               |
|          | Day 3 | 6.6 | 0.01   | 0.81  | 5.74                | 0.21               |
| 3        | Day 1 | 8.1 | –  | –   | 0.14                | 0.41               |
|          | Day 2 | 6.5 | $3.5 \times 10^{-5}$                             | 0.25  | 0.41                | 0.002              |
|          | Day 3 | 6.7 | $2.0 \times 10^{-5}$                             | 1.08  | 0.002               | 0.002              |

(–) Not estimated.

Similarly, the isotherm constants obtained from laboratory sorption experiments described the Zn concentrations in effluents rather well. The  $C_{\text{estimate}}$  of Zn in effluent 3 days 2 and day 3 were higher than corresponding  $C_{\text{before}}$  and  $C_{\text{after}}$ . This is also because the  $C_{\text{before}}$  and  $C_{\text{after}}$  of Zn could not reflect the actual Zn concentrations in above effluents. The isotherm constants obtained from laboratory sorption experiments also describe the Cr concentrations in effluent 2 quite well.

Table 5 shows that the  $C_{\text{estimated}}$  of Cu are either significantly underestimated or overestimated when the isotherm constants are obtained from chitosan sorption experiments to calculate the  $C_{\text{estimated}}$ . The presence of organic compounds in effluents may alter the copper sorption behavior onto chitosan. The isotherm constants obtained from the chitosan sorption experiment were not suitable to predict the  $C_{\text{estimated}}$  of Cu in plating effluents. To increase the accuracy of  $C_{\text{estimated}}$ , GAC was selected for alternative sorbent and the Freundlich sorption constants for Cu sorption onto GAC were obtained (Table 6). Table 5 shows that the isotherm constants based on GAC sorption experiments were more suitable to predict the copper concentrations in effluents than chitosan. Table 5 indicates that  $C_{\text{estimated}}$  of Cu were higher than  $C_{\text{before}}$  and  $C_{\text{after}}$  of Cu in effluent 3 day 3. This implies that the higher Cu concentrations might have occurred in effluent 3 day 3. The  $C_{\text{before}}$  and  $C_{\text{after}}$  for Cu in effluent 3 day 3 did not really reflect the daily Cu concentrations in the effluent. This phenomenon also occurred for Zn in effluent 3 day 3.

The presence of organic matters like chelating agents and surfactants may inhibit metal sorption onto chitosan [4,8–10] and the high metal concentrations in effluents may not be long enough to reach metal sorption equilibrium onto chitosan.

Table 6

Freundlich sorption constant for Cu sorption onto granular activated carbon

| pH | $1/n$ | $K_F$ | $r^2$ |
|----|-------|-------|-------|
| 4  | 2.763 | 0.001 | 0.919 |
| 5  | 0.362 | 0.306 | 0.974 |
| 6  | 0.395 | 0.470 | 0.916 |
| 7  | –     | –     | –     |

(–) Cu precipitated above pH 7.

Therefore, the actual highest metal concentrations in effluents should be higher than the long-time metal concentrations estimated based on sorbed metal concentrations on sorbents. Further studies should be conducted to investigate the influence of plating solution additives, such as surfactants and chelating agents on metal sorption onto sorbents.

### 3.3. Metal levels of sorbents with different sorption periods

The effluents with high (effluent 1) and low-metal concentrations (effluent 2) were selected to assess effects of metal concentrations in effluents on the accumulated metal concentrations onto chitosan.

In effluent 1, the Ni sorbed concentrations increased with sorption days (i.e.  $S_{\text{day0-3}} > S_{\text{day0-2}} > S_{\text{day0-1}}$ ), but the  $S_{\text{day0-2}}$  and  $S_{\text{day0-3}}$  of both Cu and Zn were close (Fig. 5a). It is possible that Cu and Zn concentrations in effluents were not higher than those on sequential days (Table 1). However, the  $S_{\text{day0-2}}$  and

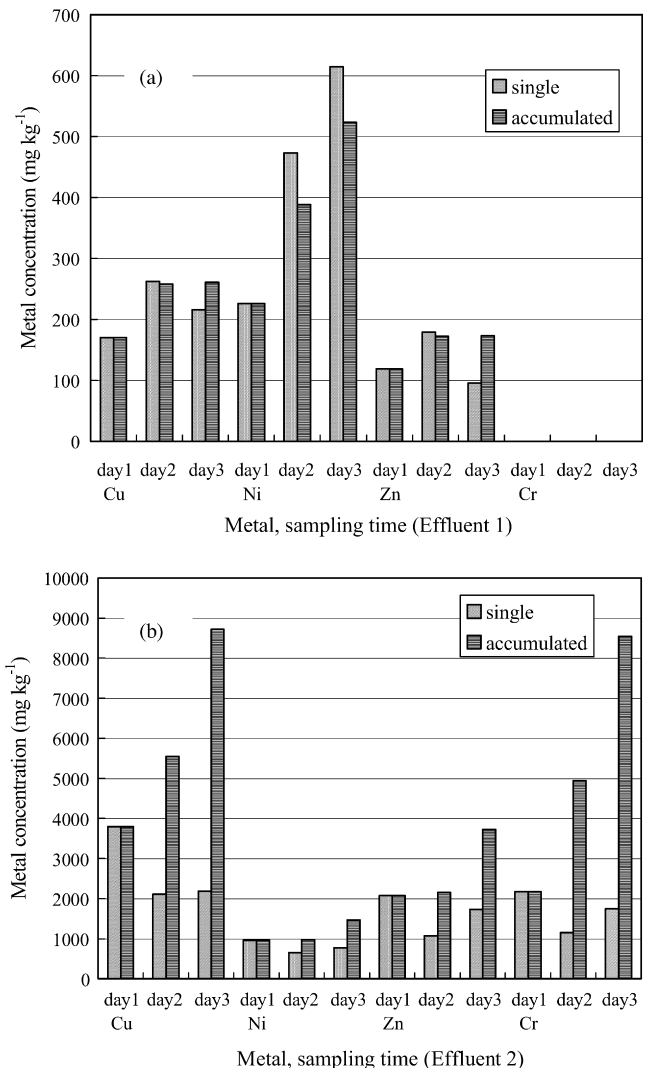


Fig. 5. The accumulated metal concentrations onto chitosan with different sorption periods (a) effluent 1, (b) effluent 2.

$S_{\text{day}0-3}$  of Ni were slightly lower than their corresponding one-day sorbed concentrations ( $S_{\text{day}1-2}$  and  $S_{\text{day}2-3}$ ). It is possible that high concentrations of organic matter like chelating agent and surfactants might have interacted with the sorption site of chitosan and thus retarded the Ni sorption onto chitosan [8,9].

In effluent 2, the sorbed concentrations of Cu, Ni, Zn and Cr increased with sorption days (Fig. 5b). However, the accumulated concentrations were much higher than their corresponding one-day sorbed concentrations on days 2 and 3 (i.e.,  $S_{\text{day}0-2} \gg S_{\text{day}1-2}$  and  $S_{\text{day}0-3} \gg S_{\text{day}2-3}$ ). The results are totally different from the accumulated sorption behavior of chitosan in effluent 1. The laboratory sorption experiment showed that the higher the metal concentrations in the solution, the longer the sorption equilibrium period (data not shown). Although it is impossible for sorption equilibrium to be reached in real effluents, the sorption kinetic is an important time factor influencing the sorbed concentrations of metals onto chitosan, especially for the effluents containing high metal concentrations. The phenomenon that the accumulated concentrations were much higher than their corresponding one-day sorbed concentrations is possibly due to shockingly high concentrations that occurred in effluents.

#### 4. Conclusions

Metal sorption of low-cost sorbents with XRF analysis was used to investigate their suitability for monitoring long-time plating effluent quality. Chitosan had higher sorption capacities for Zn, Ni, Cr and Cu than zeolite and GAC. The laboratory chitosan sorption experiment was conducted to obtain the Freundlich isotherm constants. The long-time metal concentrations were estimated by Freundlich models based on metal concentrations sorbed onto chitosan which were placed in effluents for 24 h. The comparison of results of estimated and measured metal concentrations in effluents indicated that sorbent sorption with XRF can reflect the long-term effluent quality more realistically

than daily effluent sampling. However, the XRF is a relative method to measure the heavy metal content of chitosan. Combining the XRF and the chemical analysis of effluent can provide a powerful approach to monitor the plating effluent quality.

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