



## Biosorption of chromium, copper and zinc by wine-processing waste sludge: Single and multi-component system study

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### ABSTRACT

Wine-processing waste sludge (WPWS) has been shown to have powerful potential for sorption of some heavy metals (i.e., chromium, lead and nickel) in single-component aqueous solutions. But although most industrial wastewater contains two or more toxic metals, there are few sorption studies on multicomponent metals by WPWS. This study has two goals: (i) conduct competitive adsorption using Cr, Cu and Zn as sorbates and examine their interaction in binary or ternary systems; and (ii) determine the effects of temperature on the kinetic sorption reaction. The sludge tested contained a high amount of organic matter (38%) and had a high cation exchange capacity (CEC, 255 cmol<sub>c</sub> kg<sup>-1</sup>). Infrared analysis reveals that carboxyl is the main functional group in this WPWS. The <sup>13</sup>C NMR determination indicates alkyl-C and carboxyl-C are major organic functional groups. At steady state, there are about 40.4% (Cr), 35.0% (Cu) and 21.9% (Zn) sorbed in the initial 6.12 mM of single-component solutions. Only pseudo-second-order sorption kinetic model successfully describes the kinetics of sorption for all experimental metals. The rate constants,  $k_2$ , of Cr, Cu and Zn in single-component solutions are 0.016, 0.030 and 0.154 g mg<sup>-1</sup> min<sup>-1</sup>, respectively. The sorption of metals by WPWS in this competitive system shows the trend: Cr > Cu > Zn. Ions of charge, hydrated radius and electronic configuration are main factors affecting sorption capacity. The least sorption for Zn in this competitive system can be attributed to its full orbital and largest hydrated radius. Though the effect of temperature on Zn sorption is insignificant, high temperature favors the other metallic sorptions, in particular for Cr. However, the Cr sorption is lower than Cu at 10 °C. The Cr sorption by WPWS can be higher than that of Cu at 30° and 50 °C.

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## 1. Introduction

Wastewater containing toxic metals discharged from industries, such as mining, chemicals, electroplating, alloys, pigments and battery manufacturing are dangerous to the ecology and human health. The most commonly used techniques for removing heavy metals from wastewater include biological treatment, coagulation–precipitation, ion exchange, electrolytic extraction, filtration, complexation, reverse osmosis, evaporation and adsorption. However, these techniques have certain shortcomings including high operational cost, high energy requirements, incomplete removal and generating very large amounts of sludge that requires disposal. For these reasons, there is a need to develop

low-cost processes where metal ions can be removed economically.

Adsorption is the most widely and low-cost alternative technology [1]. In recent years, some industrial and agricultural wastes, such as fly ash [2,3], activated sludge [4], clinoptilolite [5], rice hull [6], animal bones [7] and bone char [8] have been examined by using adsorption techniques for the possibility of replacing expensive sorbents, such as activated carbon.

Wine-processing generates quantities of waste sludge from the final clarifier and settling basin of wastewater treatment process, and this matter also is a significant disposal problem. Its high content of organic matter makes wine-processing waste sludge (WPWS) an excellent sorbent for removing heavy metal ions because of its high binding affinity. Most industrial wastewaters contain several species of metals, not a single component, and so the metallic sorption behaviors become more complicated than in single-component system. Thus, a sorption research for multiple metals is more realistic than for a single metal system. In multi-

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component systems, the sorption effect of heavy metal depends on surface properties of adsorbents, temperature, pH, initial metal ion concentration, dosage and the metallic species competing for binding sites [9]. The composition of a metal solution also deeply affects metal retention onto solid surfaces.

In recent years, some studies have revealed that Cr, Pb and Cu are usually more active while Ni, Zn and Cd are suppressed in a competitive adsorption system, no matter what the adsorbents are. Gomes et al. have shown that heavy metal selectivity sequences varied among soils but the most common sequence was  $\text{Cr} > \text{Pb} > \text{Cu} > \text{Cd} > \text{Zn} > \text{Ni}$  [10]. Arias et al. suggested Cu and Zn can be introduced into the soil together through the application of inorganic fertilizer, organic manure or pesticides [11]. Several studies regarding competitive adsorption concurred that Pb, Cu and Cr are more strongly retained on synthetic minerals and soil samples than Zn, Ni and Cd [12]. Jalali and Moharrami studied the competitive adsorption of trace elements in calcareous soil and reported that most sorption isotherms were well described by the Langmuir equation [13]. All soils showed greater sorption capacity and binding strength for Cu than other trace elements. Covelo et al. reported that the selectivity sequence of adsorption by four humic umbrils followed the trend of  $\text{Pb} > \text{Cr} > \text{Cu} > \text{Cd} = \text{Ni} = \text{Zn}$  [14].

The present study investigates the competitive interaction between Cr, Cu and Zn using WPWS as a sorbent. The sorption experiments were carried out in single-, binary- and ternary-component systems by kinetic methods, and the effects of temperature as well as the metallic composition on retention mechanism are evaluated. In addition, a study of WPWS aggregate was also conducted by employing Sohi's physical separation method [15].

## 2. Materials and methods

### 2.1. Samples preparation and characterization of WPWS

Rice wine-processing waste sludge was obtained from the Yilan Distillery Factory of the Taiwan Tobacco and Liquor Corporation, Taiwan. Dehydrated WPWS still contained approximately 50% moisture. The sludge was dried at 25 °C, then ground and sieved into particle size ranging from 200 to 350 mesh. The pH of WPWS suspensions at 1:2 WPWS to water ratio was determined by a pH meter. An energy-dispersive spectrometer (EDS, Kevelex level 4) was employed to examine the major elemental constituents of the sludge. Organic carbon and total nitrogen analyses were determined by an automatic elemental analysis machine (Heraeus VarioEL-III). An air-dried sample of organic matter was removed and examined with Cu K $\alpha$  radiation using a Rigaku Geigerflex X-ray diffractometer (XRD). The XRD patterns were recorded for the range of 2–60° (2 $\theta$ ) with a scanning speed of 1° (2 $\theta$ ) min<sup>-1</sup>. Predominant functional groups of WPWS were analyzed using an infrared spectrometer (Galactic Industries Corp, BIO-RAD Fis-7) by preparing the sludge pellets with KBr. To obtain further information on functional groups, WPWS samples were heated at 250, 350 and 550 °C in oven for 24 h before transparent KBr pellets were made. Organic carbon functional groups were examined by CPMAS <sup>13</sup>C NMR spectroscopy using a Bruker MSL-200 NMR spectrometer. The NMR spectra were divided into the following chemical shift regions: alkyl-C (0–45 ppm), N-alkyl-C (46–65 ppm), O-alkyl-C (65–90 ppm), acetal-C (90–110 ppm), aromatic-C (110–140 ppm), phenolic-C (140–160 ppm), and carboxyl-C (160–200 ppm) [16]. Areas of the chemical shift regions were analyzed using the Original 7.0 software package.

### 2.2. Physical separation treatment for WPWS

Sohi et al. proposed a physical separation technique which could be used to divide soil organic matter into the three constituents

of free organic matter, intra-aggregate and organomineral, according to their relative binding strength between organic matter and minerals. The term “free organic matter” represents the organic portion which had the weakest binding strength to minerals in a soil aggregate. By shaking the aggregate in a sodium iodide solution with density 1.6–1.8 g cm<sup>-3</sup> vigorously 30 s by hand, the free organic matter could be separated from the aggregate. The term “intra-aggregate” represents the organic portion binding minerals with medium strength. This portion could be separated from the aggregate which had removed the free organic matter by ultrasonic vibration treatment of 1500 J g<sup>-1</sup> over 15 min. Thirdly, after vigorous shaking as well as powerful ultrasonic treatment, the remained organic matter in aggregate was termed “organomineral”, which had the strongest binding with minerals. The detailed physical separation method was reported by Sohi et al. [15]. Similar to a soil aggregate, WPWS also consisted of organic matter and inorganic materials. However, the high content of inorganic materials in WPWS might interfere with the determinations of IR and <sup>13</sup>C NMR. Thus, the physical separation method was employed to purify the organic portion from original WPWS without destroying its natural properties. All samples obtained from physical separation process and original WPWS were used as the samples for IR and <sup>13</sup>C NMR studies. The amounts of dissolved organic carbon from WPWS particles in kinetic experiments were determined by a TOC instrument (DOHRMANN Phoenix 8000).

### 2.3. Kinetic experiments of single-component system

To conduct single-component kinetic experiments, 1.0 g of WPWS was separately added to a series of 100-mL metal solutions (Cr, Cu and Zn) with 6.12 mM of metal concentration using 200–350 mesh of WPWS at 30 °C. The initial pH of Cr, Cu and Zn solutions were adjusted at 4.0, 5.0 and 6.5, respectively, in order to avoid the formations of metal hydroxide precipitation in reactions. A 1 × 10<sup>-2</sup> M KNO<sub>3</sub> solution was applied to control ionic strength. The suspensions were agitated vigorously by a shaker with a constant speed of 110 rpm for 2 h. At the end of the desired time interval, a portion of suspension was taken from suspension immediately to filter through the 0.45- $\mu\text{m}$  membrane filter. The metal concentrations in the filtrates were determined by Inductively Couple Plasma-Optical Emission Spectrometer (ICP-OES, PerkinElmer Optima 2000 DV). The wavelengths for metal determination were respectively set at Cr (267.716 nm), Cu (327.393 nm) and Zn (206.200 nm). Argon gas was employed as the fuel. The nebulizer flow rate was controlled at 0.8 L min<sup>-1</sup> and sample flow rate was adjusted at 1.5 mL min<sup>-1</sup>. The adsorption kinetics of experimental metals were fitted using both pseudo-first-order and pseudo-second-order sorption equations. The pseudo-first-order equation can be written as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (1)$$

where  $k_1$  (min<sup>-1</sup>) is the rate constant,  $q_t$  (mg g<sup>-1</sup>) denotes the amount adsorbed at time  $t$  (min), and  $q_e$  (mg g<sup>-1</sup>) is the amount adsorbed at equilibrium. The adsorption rate constant,  $k_1$ , can be obtained from plotting  $\log(q_e - q_t)$  against  $t$ .

The pseudo-second-order equation is listed as Eq. (2):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (2)$$

where  $k_2$  (g mg<sup>-1</sup> min<sup>-1</sup>) is the rate constant.  $k_2$  and  $q_e$  can be obtained from the intercept and slope of a plot of  $t/q_t$  against  $t$ .

**Table 1**  
Mixture solutions employed for competitive kinetic sorption.

System	Solution mixture	Equivalent ratio
Binary	Cu/Zn 3.060 mM Cu/3.060 mM Zn	1:1
	Zn/Cr 3.672 mM Zn/2.448 mM Cr	1:1
	Cr/Cu 2.448 mM Cr/3.672 mM Cu	1:1
Ternary	Cu/Zn/Cr 2.295 mM Cu/2.295 mM Zn/1.530 mM Cr	1:1:1

#### 2.4. Competitive kinetic sorption

The competitive sorption studies were conducted respectively for both binary and ternary systems. According to the preliminary experiments, metal concentrations were designed for 6.12 mM and the ratio of metal A to metal B was 1:1 in equivalent for these solutions (Table 1). One gram of WPWS (200–350 mesh) was separately added to a series of 100 mL of metal mixture solutions at various temperatures (10, 30, and 50 °C). All metallic solutions were initially adjusted to pH 4.0, using NaOH and HNO<sub>3</sub>, to prevent Cr(OH)<sub>3</sub>, Cu(OH)<sub>2</sub> and Zn(OH)<sub>2</sub> precipitating in reactions, and  $1 \times 10^{-2}$  M KNO<sub>3</sub> solution was applied to control ionic strength. The suspensions were monitored with pH-stat (TIM865 Titration Manager, Radiometer Analytical). The procedure for competitive kinetic experiments is the same as that for the single-component kinetic experiment. The Cr, Cu and Zn concentrations in filtrates were determined by ICP-OES. By plotting amounts of metals sorbed versus time, the dynamic variations of metal sorption during reactions could be shown clearly.

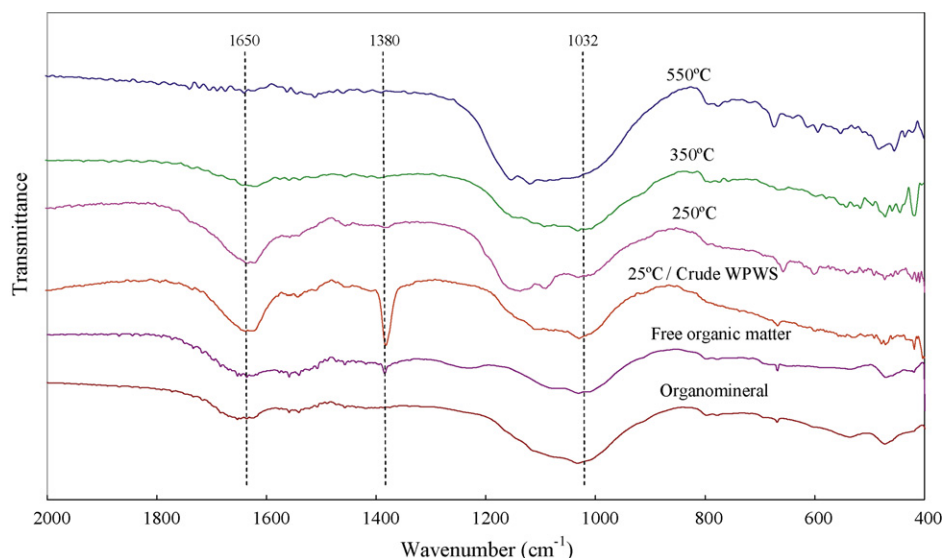
### 3. Results and discussion

#### 3.1. Characteristics and components of WPWS

The pH and CEC of crude WPWS are 6.2, and 255 cmol<sub>c</sub> kg<sup>-1</sup>, respectively. The chemical composition of WPWS is organic matter (38%), nitrogen (1.6%), phosphorus (0.06%), calcium (5.9%), iron (17%), aluminum (1.7%), manganese (0.06%), sulfur (3.0%) and silicon (5.2%). The high organic matter content and CEC of WPWS indicate a very large amount of sorption sites on the sludge. It is speculated that the iron and aluminum originated from coagulation reagents. Only trace amounts of quartz were identified by XRD analysis. The quartz originated from quartz sands, which are usually employed to prevent filter clogging when the sludge is dehydrated. During all the heat treatments, a broad IR absorp-

tion band at 1020–1150 cm<sup>-1</sup> (i.e., 1032 cm<sup>-1</sup>) can be assigned to Si–O vibration of quartz [17] (Fig. 1). Another intense absorption band appearing around 1650 cm<sup>-1</sup> can be attributed to the carbonyl stretch of ionized coordinated COO<sup>-</sup> groups [18]. Thus, we consider the ionized coordinated COO<sup>-</sup> groups as the prominent type for carboxyl groups on crude WPWS. After 250 °C heat treatment, the IR spectrum at 1650 cm<sup>-1</sup> still exhibited an intense absorption band, but it became weakened significantly at 350 °C and disappeared entirely at 550 °C. These results reveal that the carboxyl groups of WPWS are broken down rapidly when the temperature exceeds 250 °C. There was no significant IR absorption band present in the 1516 cm<sup>-1</sup> region, which is attributed to the aromatic ring C–C stretching [19]. This data reveals there are no significant aromatic structures in WPWS [20].

After physical separation treatment, only the free organic matter and organomineral fraction can be separated from the organic matter of WPWS, though it is still not known why the intra-aggregate cannot be obtained by this process. However, Sohi's method was designed for soils in the field, not for sludge. As depicted in Fig. 1, there is no significant difference in IR spectra between free organic matter and organomineral. This reveals that the absorbance band at 1650 cm<sup>-1</sup> from free organic matter has not been intensified through the separation process. It is worth noting an intense IR absorption band at 1380 cm<sup>-1</sup> that was attributed to the C–H stretch of alkyl in previous reports because it disappeared through pyrolysis of organic matter [21,22]. Nevertheless, the same IR absorption band from organomineral sample also disappeared, but without any heating treatment. Thus, we suggest this IR absorption band can be assigned to a nitrate group in WPWS [23], not the C–H stretch. The nitrate group loss from WPWS through rinsing during the physical separation process causes the band at 1380 cm<sup>-1</sup> to weaken (free organic matter) or disappear (organomineral). As shown in Fig. 2, there are significant differences in NMR spectra between all fractions of samples. The peak intensity of NMR spectrum in organomineral fraction appears to be weaker than others, indicating that a factor in high content of inorganic materials can reduce the precision in <sup>13</sup>C NMR measurement for a sludge sample. Compared with crude WPWS, the NMR spectrum shows that the 63.0, 72.9, 128.5 and 194.0 ppm peaks of free organic matter fractions have been substantially increased. The semi-quantitative of organic functional groups in WPWS shows the following trend: alkyl-C (27.0%) > carboxyl-C (20.7%) > N-alkyl-C (14.1%) > O-alkyl-C (15.8%) > phenolic-C (10.7%) > acetal-C (8.8%) > aromatic-C (2.9%).



**Fig. 1.** Infrared spectra of WPWS with different temperature treatments and after physical separation method of Sohi et al. [15].

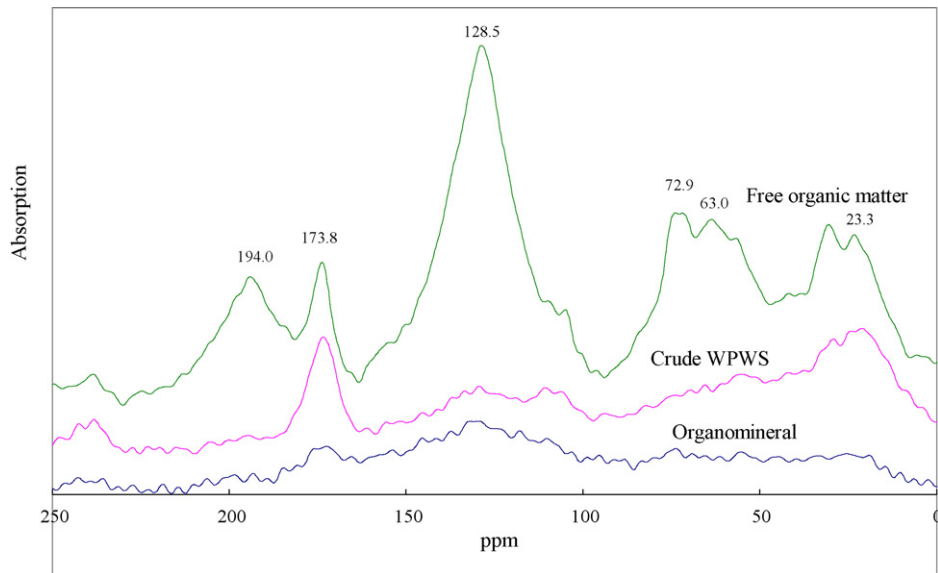


Fig. 2.  $^{13}\text{C}$  NMR spectra of WPWS after physical separation method of Sohi et al. [15].

### 3.2. Single-component kinetic sorption

Fig. 3 shows the time profiles of sorption for all experimental metals at  $30^\circ\text{C}$ . All quantities of metal sorption by WPWS increase quickly during the first 3 min of reaction, indicating that the metal ions are rapidly occupying the empty sorption sites on WPWS. Nevertheless, the Zn sorption becomes slow from the first 6 min, and the sorptions of Cr and Cu also slow down from the first 9 min as the number of the sites is decreasing. The sorptions of Cr and Cu have reach a steady state within 120 min, but this state is appears at 20 min for Zn due to its lower sorption. About 40.4% (Cr), 35.0% (Cu) and 21.9% (Zn) of the metals can be removed in such high-concentration solutions (6.12 mM). It is noteworthy that the amounts of Cr are lower than that of Cu during the first 9 min of the reaction, counter to our expectations. Similar kinetic behaviors can also been observed in a multi-component system. These three profiles show typical sorption curve for single component by WPWS. In comparison with the others, the Cr sorption is the most powerful, exhibiting a maximum curve of time profile. However, the Zn sorption exhibits a more linear relationship. According to the kinetic model, the experimental results of Cr, Cu and Zn sorption by WPWS show good compliance with the pseudo-second-order equation (all  $r^2$  are over 0.999). Thus, only the pseudo-second-order equation can be useful for this kinetic study. The rate constant ( $k_2$ ) calculated from pseudo-second-order equation for Cr, Cu and Zn sorption are  $0.016$ ,  $0.030$  and  $0.154\text{ g mg}^{-1}\text{ min}^{-1}$ , respectively.

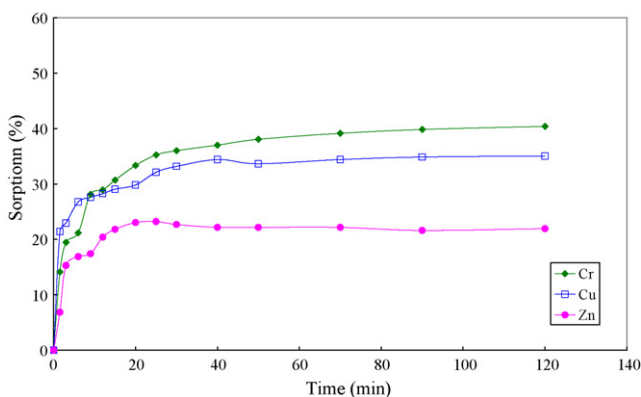


Fig. 3. Time profiles of single-component Cr, Cu and Zn sorption by WPWS at  $30^\circ\text{C}$ .

### 3.3. Multiple-components of kinetic sorption

#### 3.3.1. Binary-components of Cu and Zn

As shown in Fig. 4, Cu is much more predominant than Zn in competitive sorption, and the difference of sorption amount between Cu and Zn increases with increasing temperature. The amounts of Zn sorbed fluctuate, and this phenomenon has not been observed in the studies of single-component sorption of Zn by WPWS. This indicates that Zn sorption has been suppressed by Cu. Sorbed amounts from every sampling in each treatment have been averaged and are referred to as "sorption averages" for convenience of comparing sorption differences between various treatments. The sorption averages ( $n = 14$ ) of Cu sorption are  $0.32$ ,  $0.37$  and  $0.43\text{ meq g}^{-1}$ , and  $0.08$ ,  $0.09$  and  $0.11\text{ meq g}^{-1}$  for Zn sorption, respectively for  $10$ ,  $30$  and  $50^\circ\text{C}$  treatments. Sorption of both Cu and Zn increase with increasing operation temperature and their differences are  $0.25$ ,  $0.28$  and  $0.32\text{ meq g}^{-1}$  for  $10$ ,  $30$  and  $50^\circ\text{C}$ , respectively. This indicates such differences increase gradually with temperature rising. Owing to the inhibition from Cu sorption, the sorption curves of time profiles of Zn exhibit more linear relationship than Cu.

#### 3.3.2. Binary-components of Cr and Zn

As shown in Fig. 5, the Cr sorption predominates that of Zn in a binary system. High temperature is favorable for Cr sorption.

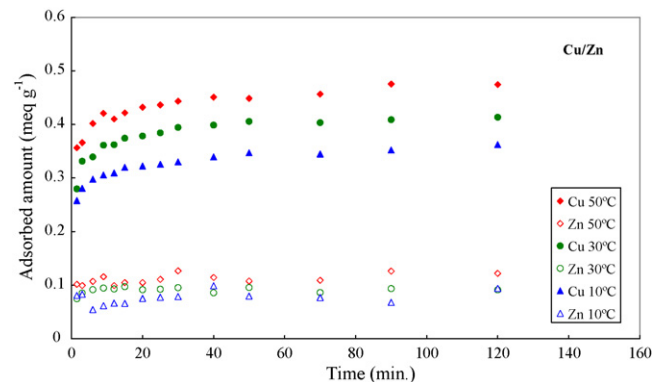
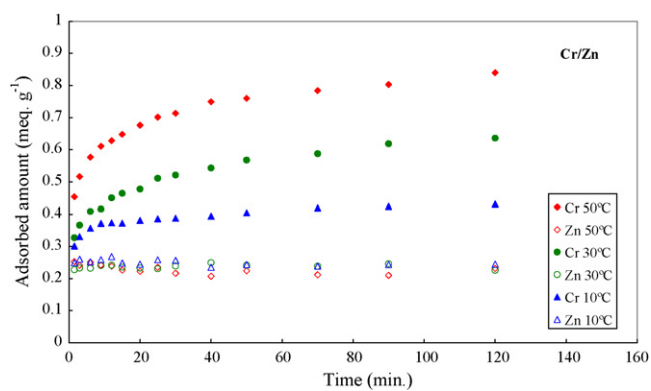


Fig. 4. Time profiles of metal sorption by WPWS in mixture of Cu and Zn at different temperatures.





**Fig. 5.** Time profiles of metal sorption by WPWS in mixture of Cu and Zn at different temperatures.

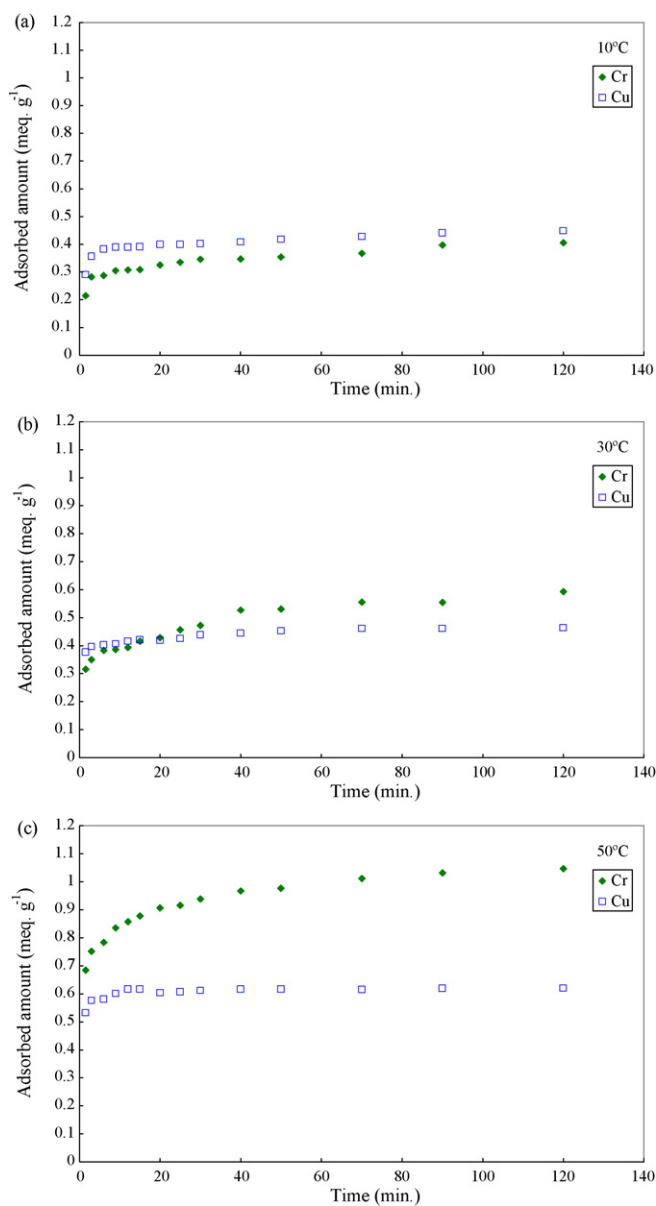
The sorption averages of Cr are 0.38, 0.49 and 0.68  $\text{meq g}^{-1}$  and 0.25, 0.24 and 0.23  $\text{meq g}^{-1}$  for Zn, respectively for 10, 30 and 50 °C treatments. Clearly, the differences of sorption amounts between Cr and Zn extend with increasing temperature, though the sorption averages of Zn remain around 0.25  $\text{meq g}^{-1}$ , regardless of the change in temperature, indicating that Zn sorption is not sensitive to increasing temperature.

### 3.3.3. Binary-components of Cr and Cu

The sorption averages of Cr and Cu are 0.33 and 0.40 for 10 °C treatment; 0.45 and 0.43 for 30 °C treatment; 0.90 and 0.60 for 50 °C treatment, respectively. In comparison with Cu, the Cr sorption is highly affected by change in temperature (Fig. 6). It is shown that the amounts of Cr sorption are lower than that of Cu at 10 °C during whole reaction (Fig. 6a). The affinity of  $\text{Cr}^{3+}$  to WPWS has been restricted at low temperature even though it has higher valence than that of  $\text{Cu}^{2+}$ . In addition, a linear time profile for Cr sorption also indicates Cr sorption is suppressed by Cu sorption at low temperature. At 30 °C treatments, the Cu sorption still dominates Cr sorption in early stages, but the Cr sorption gradually exceeds Cu sorption after 20 min of reaction (Fig. 6b). The curve of time profile for Cr sorption increases and is higher than the one at low temperature. Under increased temperature (i.e., 50 °C), Fig. 6c shows the Cr sorption has far exceeded Cu sorption, and Cr sorption become maximum, like the shape in the single-component system. This means the Cu cannot prevent the Cr ion from being sorbed onto WPWS. It can be observed there are only small differences between the initial reaction and its termination for Cu sorption. In fact, the sorption average of Cr sorption at 30 °C is 1.39 times that of the 10 °C treatment. Furthermore, the sorption average of Cr sorption at 50 °C is 1.98 times that of the 30 °C treatment. Thus, we speculate the Cu ions can rapidly occupy some empty sites on WPWS, i.e.,  $-\text{COO}^-$  while the reactions begin, but afterward, it is difficult for the free Cu ions to complex with the uncoordinated carboxyl groups, i.e.,  $-\text{COOH}$ . The Cr ions not only occupy many empty sites fast but they also can complex consistently with the uncoordinated carboxyl groups until the reaction ends at 30 and 50 °C.

### 3.3.4. Ternary-components of Cr, Cu and Zn

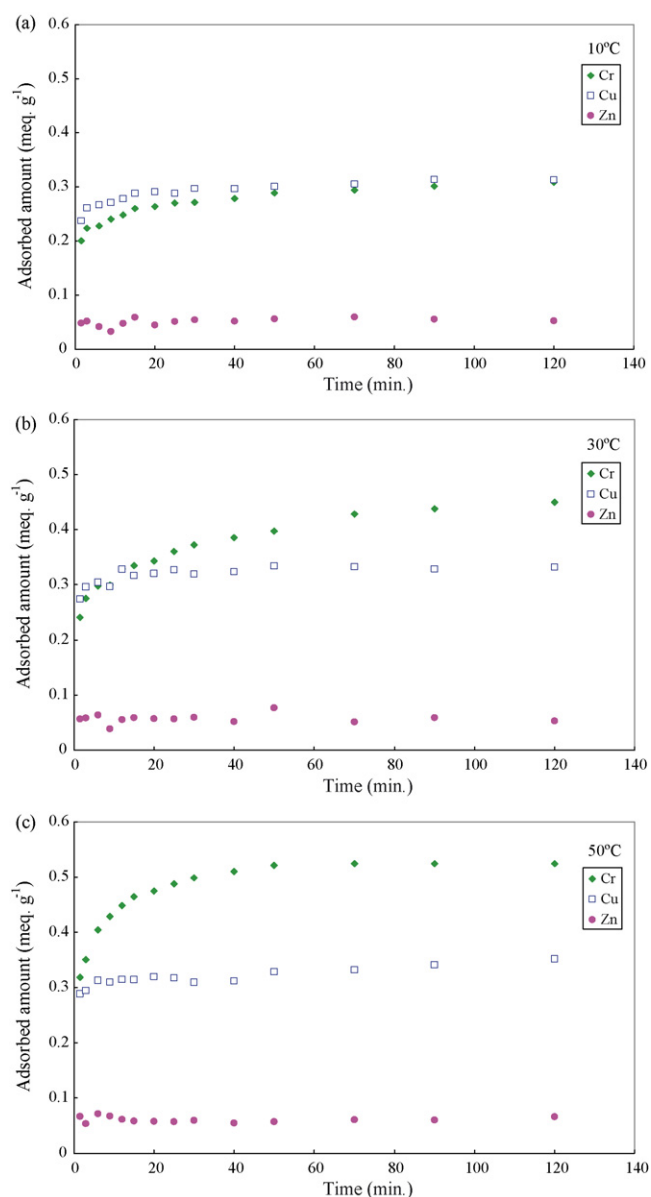
The sorption behaviors in ternary system are more complicated than in binary system. As shown in Fig. 7, temperature is the most important factor affecting the dynamic for all experimental metals, in particular for Cr. The Cr sorption by WPWS is still lower than Cu at 10 °C treatment during overall reaction (Fig. 7a); however, the amounts of Cr sorption exceed that of Cu after 15 minutes of reaction at 30 °C (Fig. 7b) and the Cr sorption is higher than that of Cu during overall reaction at 50 °C (Fig. 7c). Owing to increased temperature, the sorption amounts increase significantly for Cr sorption,



**Fig. 6.** Time profiles of metal sorption by WPWS in mixture of Cr and Cu at different temperatures. (a) 10 °C; (b) 30 °C and (c) 50 °C.

so the sorption average of Cr at 30 °C is 1.35 times as high as that at 10 °C and is 1.31 times for 50 °C higher than 30 °C. On the other hand, the sorption average of Cu at 30 °C is 1.1 times as high as that at 10 °C and is only 1.004 times for 50 °C higher than 30 °C. Curves of the Cu time profile become more linear with increasing temperature, but there is a different trend for the Cr sorption, showing bending curve with increasing operation temperature. This indicates the competitive adsorptive capacity of Cr can be clearly promoted at high temperature. Being suppressed by Cr and Cu simultaneously, sorption amounts of Zn can almost approach the maximum as soon as the reactions begin (Fig. 7a–c), after which their variations also fluctuate until the reaction ends. The sorption average of Zn at 30 °C is 1.13 times as high as that at 10 °C and is 1.07 times for 50 °C higher than 30 °C.

All the metal removal ratios in binary and ternary sorption systems are summarized in Table 2. We apply the dynamic data of competitive sorption into pseudo-first-order and pseudo-second-order sorption equations. All sorptions relevant to Cr, Cu and Zn sorption show a good correlation with pseudo-second-order model



**Fig. 7.** Time profiles of metal sorption by WPWS in mixture of Cr, Cu, and Zn at different temperatures. (a) 10 °C; (b) 30 °C and (c) 50 °C.

in either binary or ternary system (Table 2). Thus, a pseudo-second-order model can be used to predict and control the amounts of metals removed when WPWS is employed to treat the mixture solutions of Cr, Cu and Zn. In kinetic experiments, the final dissolved organic carbon are 42.4 (10 °C), 53.0 (30 °C) and 84.6 (50 °C) mg L<sup>-1</sup>. The phenomenon indicates the organic structure of WPWS was changed when the temperature rose. Thus, we speculate the

**Table 2**

Metal removal ratios (%) and determination constants ( $r^2$ , in parenthesis) of pseudo-second-order model in competitive sorption of Cr, Cu and Zn by WPWS at different temperatures.

Cr/Cu	10 °C	30 °C	50 °C	Cr/Zn	10 °C	30 °C	50 °C
Cr	45.7 (0.995)	66.9 (0.995)	96.6 (0.999)	Cr	51.4 (0.999)	75.8 (0.995)	100.0 (0.997)
Cu	53.6 (0.999)	55.6 (1.000)	63.7 (1.000)	Zn	26.5 (1.000)	24.4 (0.997)	25.0 (0.996)
Cu/Zn	10 °C	30 °C	50 °C	Cr/Cu/Zn	10 °C	30 °C	50 °C
Cu	53.1 (0.999)	60.6 (1.000)	69.5 (0.999)	Cr	58.7 (0.999)	85.8 (0.996)	100.0 (1.000)
Zn	13.0 (0.962)	12.6 (0.998)	16.9 (0.994)	Cu	57.2 (1.000)	60.5 (1.000)	64.2 (0.998)
				Zn	9.4 (0.994)	9.5 (0.983)	11.9 (0.994)

**Table 3**

Dissociation constants of organic acids with Cr, Cu and Zn, respectively [25].

Organic acids	Cr <sup>3+</sup>	Cu <sup>2+</sup>	Zn <sup>2+</sup>
Oxalic acid	5.34 ( $K_1$ )	4.85 ( $K_1$ )	3.44 ( $K_1$ )
	5.17 ( $K_2$ )	4.36 ( $K_2$ )	3.04 ( $K_2$ )
Citric acid	5.55 ( $K^d$ )	3.3 ( $K^d$ )	–
		5.9 ( $K_1$ )	4.98 ( $K_1$ )
Acetic acid	5.03 ( $K^b$ )	–	–
		1.89 ( $K_1$ )	1.28 ( $K_1$ )
		1.20 ( $K_2$ )	0.81 ( $K_2$ )
Malic acid	–	2.00 ( $K^c$ )	1.66 ( $K^c$ )
		3.24 ( $K^d$ )	2.93 ( $K^d$ )

L: ligands; M: Metals;  $K_1$ :  $M + L \rightleftharpoons ML$ ;  $K_2$ :  $ML + L \rightleftharpoons ML_2$ ; a:  $Cr^{3+} + H_3L \rightleftharpoons CrL + 3H^+$ ,  $Cu^{2+} + H_3L \rightleftharpoons CuHL + 2H^+$ ; b:  $CrL^{2+} + 2L^- \rightleftharpoons CrL_3$ ; c:  $Cu^{2+} + H_2L \rightleftharpoons CuH_2L^{2+}$ ,  $Zn^{2+} + H_2L \rightleftharpoons ZnH_2L^{2+}$ ; d:  $Cu^{2+} + HL^- \rightleftharpoons CuHL^+$ ;  $Zn^{2+} + HL^- \rightleftharpoons ZnHL^+$ .

sludge aggregates became loose and more carboxylic groups began immersing liquid phase and this led to the increase of sorption site at higher temperature. However, Cr or Cu had the priority filling the sites full. The Zn could occupy hardly the sites due to their competition in multicomponent system.

### 3.4. Sorption background between metals and WPWS

The sorptions of Cr, Cu and Zn by WPWS in mixtures follow the trend: Cr > Cu > Zn. McBride reported that selective adsorption of Cr, Cu and Zn are related to their susceptibility to hydration, charge/radius ratio and electronegativity [24]. Compared with Cu and Zn, the Cr ion has the highest valence and smallest hydrated radius, so it can bind tightly with negative-charged functional groups. The difference of ionic radius between Cu<sup>2+</sup> (0.73 Å) and Zn<sup>2+</sup> (0.74 Å) is very small, though such difference extends 10 times between their hydrated ionic radii (2.06 Å for Cu<sup>2+</sup> and 2.16 Å for Zn<sup>2+</sup>). It is physically more difficult for hydrated ions with larger volume to approach the center in sorption sites. The electron configuration of Cr<sup>3+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> can be represented as [Ar] 3d<sup>3</sup>4s<sup>0</sup>, [Ar] 3d<sup>9</sup>4s<sup>0</sup> and [Ar] 3d<sup>10</sup>4s<sup>0</sup>, respectively. This shows the 3d<sup>10</sup> orbital of Zn<sup>2+</sup> is full and there is no empty orbital for it to form strong bonding or induced dipole moment with negative-charged functional groups. Therefore, the affinity for Zn to WPWS is weak, so Zn sorption amounts are far lower than that of Cr and Cu. A transient metal, with smaller ionic radius and empty orbital, is easier to complex with organic materials. Oxalic, citric, acetic and malic acid are not only important materials in metabolism but also abound in organic matter. The carboxyl functional groups in WPWS complexed with metals are related to its pK values. The dissociation constant (pK) of these organic acid with metals can be regarded as the strength of bonding with carboxylic groups. As the pK value is higher, this bonding will be stronger. It can be observed from Table 3 that all pK<sub>1</sub> and pK<sub>2</sub> values are higher for Cu<sup>2+</sup> than Zn<sup>2+</sup>.

#### 4. Conclusions

This study of single-component aqueous solutions has shown wine-processing waste sludge to be an effective sorbent for removing Cr, Cu and Zn in aqueous solutions. Nevertheless, the Zn sorptions in mixture solutions are suppressed significantly by competition with others. The characteristics of high CEC and organic matter contents reveal there are a great many sorption sites in WPWS. Carboxyl is the most important functional group and also the most available site attracting metals in WPWS. Only free organic matter and organomineral have been recognized for WPWS by Sohi's fractionations. The  $^{13}\text{C}$  NMR studies for organic functional groups of WPWS can be improved substantially by Sohi's physical separation method, but it is insignificant for IR studies. High temperature favors sorption of all metals, but it is more favorable for Cr. The sorption behaviors of Cr, Cu and Zn fit well with a pseudo-second-order model for single, binary and ternary systems. Hydrated ionic radius and electron configuration are important factors which can affect the sorption capacity for a transient metal on WPWS. Zinc has a larger hydrated ionic radius and a filling electron configuration, so it shows the least sorption. Clearly, the temperature affects the sorption behaviors of experimental metals. We consider a good control on temperature is needed to obtain ideal results for metal removal when treating a multi-component system. It is not clear why the Cr sorption is so ineffective at  $10^\circ\text{C}$  in the Cr/Cu system, and this merits further study.

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