

# In situ XANES study of removal of heavy metals from laboratory wasteliquid by the ferrite process

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## Abstract

Heavy metals in the laboratory wasteliquid can be recovered as stable and economic ferrite by the ferrite process. The spectrum of X-ray absorption near edge structure (XANES) specifically shows that 92% of  $\text{Cr}(\text{OH})_3$  and 8% of  $\text{CrCl}_2$  in the original laboratory wasteliquid are converted to 70% of  $\text{Cr}_2\text{O}_3$  and 30% of  $\text{CrCl}_2$  in the precipitates by the ferrite process. The concentrations of total chromium, lead and zinc in the laboratory wasteliquid also dropped from 383,000, 20.9 and 277 ppb, respectively, to lower than the effluent standards of the Environmental Protection Administration (EPA) in Taiwan. The XRD (X-ray diffraction) analysis shows that the chromium ferrite is achieved at  $\text{pH} > 9$ . On the other hand, the XANES spectra of the in situ experiment show there were 52% of  $\text{Fe}_3\text{O}_4$  in the precipitates.

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## 1. Introduction

Campus laboratories commonly use highly hazardous chemicals for teaching and research. Laboratory wasteliquids are of multiple varieties, scarce quantities, ambiguous classifications and are often unidentifiable, which makes it far more difficult for contractors to dispose of them. Most administrators of laboratory wasteliquid use storage tanks to store the wasteliquid residues left from experiments. Within a few years, this waste will become a serious problem on university campuses. Many schools will have to encounter it and wait for an effective solution.

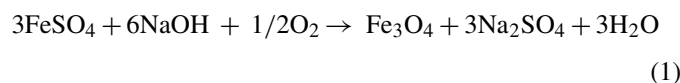
Metals are probably the oldest toxins known to humans. Most metals affect multiple organ systems, causing disorders such as hypersensitivity, conjunctivitis, asthma, or even systemic anaphylaxis. Chromium is an abundant element in the earth's crust and occurs in oxidation states ranging from  $\text{Cr}^{2+}$  to  $\text{Cr}^{6+}$ , but only trivalent and hexavalent forms are of biological significance. The trivalent is the more common form. The major effect from ingestion of high levels of chromium is acute tubular and glomerular

damage. Evidence of kidney damage from lower level chronic exposure is equivocal. Hexavalent chromium is corrosive and causes chronic ulceration and perforation of the nasal septum. Trivalent chromium compounds are considerably less toxic than the hexavalent compounds and are neither irritating nor corrosive [1]. Lead is the most ubiquitous toxic metal and is detectable in practically all phases of the inert environment and in all biological systems. Because it is toxic to most living things at high exposures and there is no demonstrated biological need for it, the major issue regarding lead is determining the dose at which it becomes toxic. The most sensitive effects of lead in infants and children involve the nervous system [2–4]. The critical effect for adults in the general population may be hypertension [2]. Zinc is a nutritionally essential metal and a deficiency results in severe health consequences. Zinc does not accumulate with continued exposure but body content is modulated by homeostatic mechanisms that act principally on absorption and liver levels. With regard to industrial exposure, metal fume fever resulting from inhalation of freshly formed fumes of zinc presents the most significant effect [5–7].

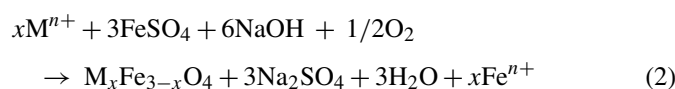
Many methods, such as ion exchange, adsorption, metal hydroxide precipitation and reverse osmosis can be used to remove heavy metals from wastewater [8,9]. A less commonly used technique is the ferrite process. In the ferrite process,

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heavy metals could be removed from wastewater by forming stable and magnetic precipitates. They are potential use of the recovered ferrites commercially in various industrial applications [10]. Ferrites are iron oxide compounds always contain at least one other metallic ion. It may be expressed as  $M_xFe_{3-x}O_4$  where M may be Ni, Mn, Mg, Zn, Cu or Cr, are ferromagnetic materials. A small external magnetic field is able to reorganize the sublattices of ferrite and change their internal magnetic moments. It appears that heavy metal can be attracted in a magnetic field according to the degree of magnetic permeability [11–13]. It is of great usage in treating the metal-rich wastewater [14–19]. Ferrus is partially oxidized by air to produce  $Fe_3O_4$  in an alkaline solution. The reaction is shown in Eq. (1) below [15]:



When the solution contains other metals ( $M^{n+}$ ), these metals may occupy the positions of some  $Fe^{2+}$  and  $Fe^{3+}$  in the magnetite structure. The reaction is shown in Eq. (2) below [15]:



XANES spectroscopy is very useful in the identification of elements within a different environment. In the XANES regime, multiple scattering of the excited electron confers sensitivity to the details of the spatial arrangement of atoms neighboring the absorbing one; not only their radial distances but also their orientations relate to one another, as well as to bond angles [20]. In this study, the effect of pH on the ferrite formation in the complex laboratory wasteliquid was investigated and XANES could be used to observe the change of valence of chromium compounds as well as the behavior of ferrite formation in the process.

## 2. Experimental

### 2.1. Materials

The laboratory wasteliquid was obtained from some universities in Tainan. The chemicals ( $FeSO_4 \cdot 7H_2O$ , NaOH) used were of an analytical grade.

### 2.2. Apparatus

Many apparatuses were used in this experiment, such as a pH meter (Metler Toledo, InLab 415), an oven (Mettler), an oxidation–reduction potentials meter (Metler Toledo), a heater (Thermalyne, Cimarec3), a vacuum filtration apparatus, filter paper (125 mm diameter), a thermal control meter (Fargo Instruments, CA-400) and an XRD (Siemens, D5000).

XANES spectra of the samples and  $Fe_3O_4$  (ferrite) were recorded on the Wiggler beam line of the National Synchrotron Radiation Research Center (NSRRC) in Taiwan.

### 2.3. Procedure

The laboratory wasteliquid was mixed with a [ $Fe^{2+}$ /total metal] mole ratio of 20:1 in the beaker. When mixed thoroughly, a digital pH meter was used to monitor the pH of laboratory wasteliquid. It was adjusted between 5, 7, 9 and 11 by adding a 1N sodium hydroxide solution. The contents of the baker were heated by water bath at 70 °C. At the same time, the laboratory wasteliquid was aerated (the aeration rate was 4 L/min), by stirring at 150 rpm for 20 min and 30 rpm for 60 min. An ORP meter was used to monitor the oxidation–reduction potentials. The precipitates formed were separated from the liquid phase by a vacuum filtration apparatus and put into the oven at 105 °C for 8 h. The filtrate and the precipitates were subjected to inductively coupled plasma (ICP) analysis. The precipitates were also analyzed by XRD and in situ XANES. The sample was detected on-line during the ferrite process. The original laboratory wasteliquid and the sludge generated from the laboratory wasteliquid by the ferrite process were measured after 20 and 60 min. The absorption edge was determined at the half-high (precisely determined by the derivative) of the XANES spectrum after pre-edge baseline subtraction and normalization to the maximum post edge intensity. Principal component (factor) analysis (PCA) was used in the data treatment to optimize the quantitative extraction of relative concentrations. Structure of ferrite compound was determined by X-ray diffraction spectroscopy (Siemens, D5000) with a Cu  $K_\alpha$  radiation. Generally, a sample was scanned from 10° to 80° ( $2\theta$ ) with a scan rate of 4°/min. The specific peak intensities and  $2\theta$  values were recorded and identified by a computer library system.

## 3. Results and discussion

The chromium XANES spectra (Fig. 1) of the original laboratory wasteliquid and the precipitates generated from laboratory wasteliquid by ferrite process were compared with reference spectra arising from known Cr compounds. The shape of the edge and the pre-edge region resonances are characteristic for the local symmetry of the investigated atom sites [21–23]. A single intense pre-edge peak (at 5994 eV) can be used as a fingerprint for tetrahedrally coordinated Cr atoms [22,23]. This typical isolated pre-edge resonance which arises from a 1s–3d transition is present in the spectra of reference  $Cr(OH)_3$  and original laboratory wasteliquid (Fig. 1(a)). On the other hand, the spectra of the reference  $Cr_2O_3$  and precipitates (Fig. 1(b)), where Cr atoms occupy octahedral sites in the lattice, exhibit two small resonances in the pre-edge region. They can be assigned to transitions of 1s electron into unoccupied valence orbitals with octahedral symmetry, and are characteristic for octahedrally coordinated Cr materials [22,23]. Fig. 1(a) also shows that there were 92% of  $Cr(OH)_3$  and 8% of  $CrCl_2$  in the original laboratory wasteliquid. After the ferrite process,  $Cr(OH)_3$  was converted to 70% of  $Cr_2O_3$  and 30% of  $CrCl_2$  in the precipitates (see Fig. 1(b)).

Fig. 2 shows that the recovery efficiencies of total chromium, lead and zinc ions were excellent. The recovery rate of total chromium, lead and zinc ions achieved 99.0% at pH > 9. The effectiveness achieved by using the ferrite process to remove

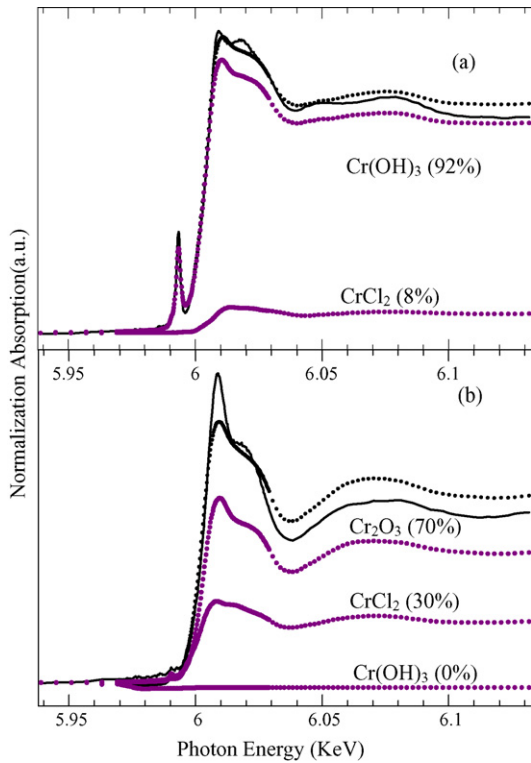


Fig. 1. Chromium XANES spectra of (a) original laboratory wasteliquid and (b) the precipitates generated from laboratory wasteliquid by ferrite process.

heavy metals from laboratory wasteliquid was especially obvious, with total chromium dropped from 383,000 to 2.93 ppb, lead from 20.9 ppb to non-detected and zinc from 277 to 1.30 ppb in the filtrate at pH 9. Each of them was in accordance with the effluent standards of the EPA in Taiwan.

Fig. 3(a) shows the X-ray diffraction pattern of the standard spectrum of  $\text{Cr}_2\text{FeO}_4$ . Fig. 3(b)–(d) also shows the characteristic spectrum of precipitates generated from laboratory wasteliquid at various pH values. It is worth mentioning that though the recovery rate of heavy metal at pH 7 was higher than 96%, the  $\text{Cr}_2\text{FeO}_4$  was absent in the precipitates as shown in Fig. 3(b), whereas the  $\text{Cr}_2\text{FeO}_4$  was formed when pH was higher than 9. It seems that  $\text{pH} > 9$  could be the best condition for the formation of ferrite. In the meantime, the concentration of lead and zinc in the precipitates are rare. The XRD data of precipitates for lead and zinc are out of detecting limited.

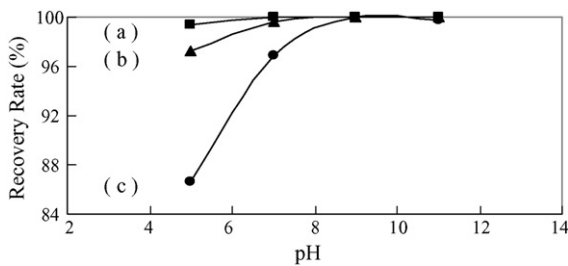


Fig. 2. The recovery rate of heavy metals, (a) total chromium, (b) lead and (c) zinc from laboratory wasteliquid by the ferrite process at various pH values. Recovery rate%=(the quantities of total chromium, lead and zinc ions in the precipitates)/(total quantities of heavy metals in laboratory wasteliquid).

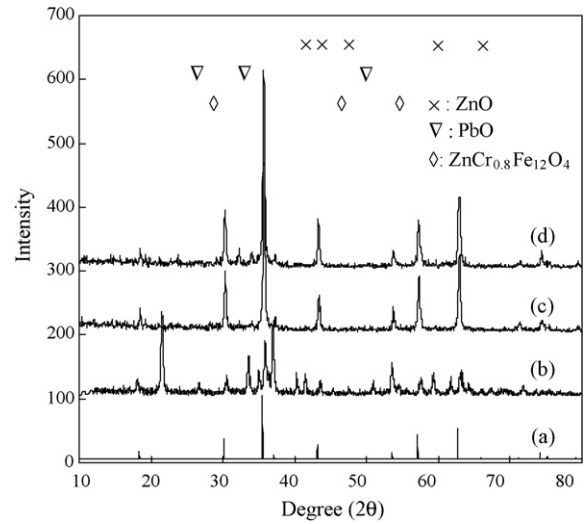


Fig. 3. X-ray diffraction pattern of (a) the standard spectrum of  $\text{Cr}_2\text{FeO}_4$ , and precipitates collected from laboratory wasteliquid at various pH values, (b) pH 7, (c) pH 9 and (d) pH 11.

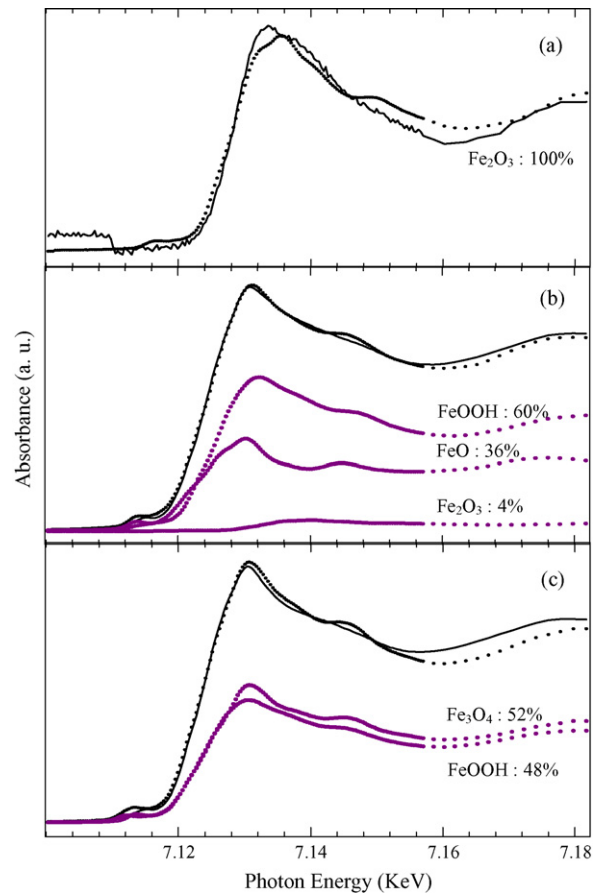


Fig. 4. In situ XANES spectra of (a) original laboratory wasteliquid, (b) sludge generated from laboratory wasteliquid by the ferrite process after 20 min of flocculation and (c) the sludge generated from laboratory wasteliquid by the ferrite process after 60 min of flocculation.

Although, the XRD pattern showed that the optimize condition for ferrite formed in  $\text{pH} > 9$ . The several of iron ions during the ferrite process were still not clear. The XANES spectra of the in situ experiment at  $\text{pH} 9$  were done for this purpose. Fig. 4(a) shows that most of  $\text{Fe}^{3+}$  ions were in the original laboratory wasteliquid. Then the laboratory wasteliquid was mixed with a  $[\text{Fe}^{2+}/\text{total metal}]$  mole ratio of 20:1 at  $\text{pH} 9$ . Fig. 4(b) shows that an expanded pre-edge region where the spectral changes are also consistent with structural transformation from  $\alpha\text{-Fe}_2\text{O}_3$ -like to 60% of  $\text{FeOOH}$ , 36% of  $\text{FeO}$  and 4% of  $\text{Fe}_2\text{O}_3$  in the precipitates after 20 min of flocculation. This  $1s \rightarrow 3d$  electric-dipole transition gains additional intensity when the iron center is in a non-centrosymmetric environment or through mixing of iron 3d orbitals with 4p ones [24]. Fig. 4(c) also shows that 52% of ferrite can be found in the precipitates after 60 min of flocculation. Therefore, the ratio of  $[\text{Fe}^{2+}/\text{Fe}^{3+}]$  was another important factor of the ferrite formation.

#### 4. Conclusions

The ferrite process can effectively remove heavy metals from laboratory wasteliquid. The concentrations of total chromium, lead and zinc in the wasteliquid were reduced to the effluent standards of the EPA in Taiwan. However, XRD data show that  $\text{Cr}_2\text{FeO}_4$  would be formed at  $\text{pH} > 9$ . The XANES spectra of the in situ experiment also show there were 52% of  $\text{Fe}_3\text{O}_4$  in the precipitates. It seems that  $\text{pH} > 9$  is the best condition for the formation of ferrite. In this study it is suggested that the ferrite process could be applied to remove heavy metals from laboratory wasteliquid and therefore solve the serious problem of waste storage on university campuses. On the other hand, the wastes may be regenerated as Cr-ferrites, which could be reused and recycled.

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