



Oxidation of high iron content electroplating sludge in supercritical water: stabilization of zinc and chromium

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Abstract

The stabilization of heavy metals (zinc and chromium) and the degradation of organic pollutants during supercritical water (SCW) and supercritical water oxidation (SCWO) treatment of electroplating sludge (EPS) with a high iron content were studied. Experiments were performed in a batch reactor at temperatures in the range from 623.15 to 823.15 K with an oxygen coefficient (OE) from 0 to 2.0, a reaction time of 7 min and pressure of 25 MPa to examine the effect of the operation conditions. Chemical oxygen demand (COD) and total organic carbon (TOC) in raw sludge and liquid products under different reaction conditions were detected. The results indicated that more organic pollutant degradation occurred under supercritical conditions than in subcritical water. Additionally, as the temperature and amount of oxidant increased, the organic pollutant removal rate increased. In addition, the Zn and Cr removal efficiency from sludge was more than 98% under all conditions. Temperatures under 773.15 K had a positive effect, whereas the oxygen ratio was more significant than the other factors above 773.15 K. Furthermore, leaching toxicity tests of the heavy metals in solid products were conducted based on the toxicity characteristic leaching procedure (TCLP). All heavy metals showed greatly reduced leaching toxicity due to their stabilization. The Zn in the EPS is more easily converted into a solid product after SCWO treatment; however, Cr is more difficult to leach from the solid product. Oxides of iron, zinc, and chromium were detected by X-ray diffraction and an electron probe microanalyzer, and the yield of the oxides increased with increasing temperature and oxidant amount. Using the obtained data and analysis results, the effect of Fe on the stabilization of Zn and Cr was studied.

Keywords Electroplating sludge · High iron content · SCWO · Zinc · Chromium · Stabilization mechanism

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Introduction

Electroplating sludge (EPS) is the main pollutant produced by electroplating wastewater treatment in electroplating enterprises. Several million tons of EPS are produced by electroplating enterprises annually in China. The heavy metal and organic pollutant contents in EPS greatly exceed the national environmental emission standards in China and are included in China's national hazardous waste list. If EPS is allowed to sit for a long time, the harmful substances in EPS will migrate, which will lead to serious secondary pollution (Espinosa and Tenório 2001). For the treatment of hazardous waste, conventional treatment methods, such as landfill, incineration, chemical leaching extraction, and bioleaching, have some disadvantages. These methods, to varying degrees, have problems such as incomplete treatment, secondary pollution, complex treatment processes, high treatment costs, and long cycles (Saxena and Jotshi 1996; Jensen and Jepsen 2005; Jakob et al. 1995).

In the field of heavy metal pollutant removal, researchers have developed new technologies. Huang et al. (2016) and Xue et al. (2018a, b, c) used rhamnolipid (RL)-stabilized nanoscale zero-valent iron (RNZVI) and tested its potential performance for changing the mobility and speciation of cadmium (Cd) and lead (Pb) in river sediments; based on the influences of the microbial community and organic carbon (OC), the authors discovered that the abiotic (i.e., from the reaction with NZVI) and biotic processes fueled by RNZVI lead to the immobilization of Cd and Pb in river sediments. Supercritical water oxidation (SCWO) is a rapid, thorough treatment method that produces no secondary pollution and has a small footprint. This method is considered a promising, efficient end-of-pipe treatment technology that can degrade almost all kinds of organic compounds in a short time, and the main products are environmentally friendly CO₂ and H₂O (Brunner 2009; Chen et al. 2015; Gong et al. 2016; Bermejo and Cocero 2010; Veriansyah et al. 2007). Since SCWO technology has the advantages mentioned above, research on SCWO technology has increased. SCWO of organic pollutants, such as N-containing heterocyclic hydrocarbon waste, landfill leachate, 2-3-4-nitroaniline, trimethyl phosphate, and heteroatoms in heavy oil, and the properties of catalysts in SCWO have been extensively studied (Al-Duri and Alsoqyani 2017; Apj et al. 2018; Yang et al. 2018; Kosari et al. 2018; Hosseinpour et al. 2018). SCWO of heavy metal pollutants can separate heavy metals from organic wastes in the form of insoluble oxides and salts (Yoko and Oshima 2013; Zou et al. 2013, 2015). Zhen et al. (2000) found that 97.6% of Cd, 87.3% of Cr, and 100% of Pb in deinked waste changed from soluble to insoluble substances during SCWO treatment at 798.15 K and 30.6 MPa. In addition, CdO, CdCO₃, CrO₂, HCrO₂, PbCrO₄, PbCO₃, and PbO_x were identified in the solid products. Veriansyah et al. (2005) studied and found in situ formation of chromium oxide nanoparticles (α -HCrO₂ and Cr₂O₃) due to decomposition of ammonium dichromate in the wastewater, and nonfaceted crystalline chromium particles were obtained with sizes in the range of 200–400 nm during SCWO treatment. Bo et al. (2009) conducted sequential extraction experiments, and the results showed that SCWO treatment can stabilize heavy metals in Fe–Mn oxides and residual fractions. However, acidic ash must be neutralized to near neutral conditions before SCWO treatment to effectively stabilize the hazardous elements in the ash. Wang et al. (2012) studied SCWO treatment of medical waste incineration (MWI) fly ash with PCBs at 648.15 K and 30 min; the degradation of PCBs can be catalyzed by the heavy metal components in MWI fly ash, resulting in over 90% degradation. Zou et al. (2013) studied SCWO treatment and observed that more than 98% of Cr was recovered from sludge in the resultant ash under all conditions; the chromium recovered in the solid ash was amorphous at 773.15 K. Additionally, the leaching toxicity of heavy metals such as

Cr was greatly reduced through stabilization. In recent years, Chen et al. (2016) reported that heavy metals in simulated wastewater can be deposited in the form of superfine particles and that Cr can be converted into superfine Cr₂O₃. Chen et al. (2017) studied the transformation behaviors of Pb, Cd, Mn, Cu, and Zn in lignite during SCW gasification and determined their transformation pathways. Yao et al. (2018) discovered that Ba, Cr, and Pb in oil-based drilling debris were almost all stabilized in solid products after SCWO treatment, and the maximum Zn and Cu contents in the liquid products were 1.2% and 4.5%, respectively, after SCWO treatment at 748.15 K for 2 min with OE 2.5. However, the effect of high iron content on the stabilization of Zn and Cr in EPS after SCWO treatment and an analysis of the solid products from SCWO treatment have rarely been reported.

As a typical hazardous waste with a high concentration of organic and heavy metal pollutants, EPS cannot currently be properly and efficiently disposed. In contrast to conventional EPS, the iron content of the EPS in this study is high. Due to limited storage space and secondary pollution, it is difficult to treat this EPS with the curing and incineration methods commonly used at present (Li et al. 2010; de Souza E Silva et al. 2006; Peng and Tian 2010). Furthermore, an efficient and clean treatment technology for EPS needs to be developed. The lack of a waste treatment method is a limiting factor for the development of the electroplating industry and is an urgent problem for researchers to solve. Hence, experiments were conducted to (1) ascertain the removal efficiency of organic pollutants and the migration and transformation of heavy metals; (2) investigate the composition and structure of solid ash, as well as the leaching characteristics of Fe, Zn, and Cr; and (3) understand the effect and mechanism of Fe on the stabilization of Zn and Cr. Thus, this study provides new support for other similar pollutants with high iron content.

Experimental section

Materials

The EPS sample was sludge produced by the pressure filtration treatment after the addition of iron flocculant into electroplating mixed wastewater from an electroplating enterprise located in Tianjin, China. The sludge has a complex composition and contains a variety of organic and heavy metal pollutants. The physical and chemical properties of the sludge are shown in Table S1.

Apparatus and experimental methods

The internal volume of the batch reactor was 200 mL, and the temperature and pressure were 873.15 K and 32 MPa,

respectively. The material of the reactor was C276 alloy. The experimental apparatus is presented in Fig. S1.

First, the calculated amounts of sludge and hydrogen peroxide (the OE is defined as the ratio of the added oxygen content to the COD content of the sludge) were added to the reactor. After quickly sealing the top cover and opening the exhaust valve, nitrogen was used to purge the reactor chamber, and the air inside the reactor was discharged to prevent excess oxygen in the air from participating in the reaction. Subsequently, the reactor was heated at a speed of 10 K/min, and the pressure inside the reactor was monitored by a pressure sensor. The reaction time is to the time after the target experimental temperature was reached, and the heating time is not included. Both the reaction time and the target reaction temperature were set using the temperature control system. After the experiment, the reactor chamber was taken from the furnace and cooled to room temperature. Then, the lid was opened to remove the liquid product, which was saved, and the volume of the liquid was recorded. The solid phase product was washed out of the reactor chamber with ultrapure water, dried at 378.15 K, and then saved for further tests. Because the reaction time and pressure had little influence on the experimental results, the reaction pressure and time in this study were set as constant values of 25 MPa and 7 min, respectively.

Analytical methods

COD measurements were conducted by a water quality analyzer (HACH, DR 3900). Inductively coupled plasma mass spectrometry (Plasma Quant MS, Analytik Jena AG) was used to detect metal concentrations. The concentrations of heavy metals leached from solid products were determined based on the TCLP analysis (Toxicity Characteristic Leaching Procedure, EPA method 1311). The TCLP is widely used in China and the USA to determine the leachability and mobility of heavy metals in solids in the environment. The metal oxide content in the solid residue was determined using an electron probe microanalyzer (JXA-8230, JEOL). The morphology of the solid products was observed by a field emission scanning electron microscope (SU5000, HITACHI). An X-ray diffractometer (Ultima IV, RIGAKU) was used to analyze the main components of the solid products.

Results and discussion

Degradation of organic pollutants

EPS is often treated as hazardous waste due to its high content of organic pollutants. However, the high content of organic compounds in the sludge provides an excellent resource for SCWO and energy recovery. Due to the complex and difficult classification of the organic components, the degradation of

the organic compounds in the EPS was reflected as the concentration of TOC and COD degradation efficiency (COD degradation efficiency = $(1-a) \times 100\%$, a is defined as the concentration of COD in the liquid products under a certain reaction condition divided by the concentration of COD in the raw sludge), initial value, and final value. The COD degradation efficiency in liquid products under different reaction conditions is shown in Fig. 1. The concentration of TOC in liquid products under different reaction conditions is shown in Table S2.

Previous reports have noted that the degree of organic pollutant degradation in SCWO mainly depends on the temperature and OE. Therefore, the effects of the temperature (623.15, 673.15, 723.15, 773.15, and 823.15 K) and OE ($n=0, 0.5, 1.0, 1.5,$ and 2.0) on the reaction were studied, and the pressure and time for each experimental condition were 25 MPa and 7 min, respectively. As shown in Fig. 1, the maximum COD degradation efficiency was only 16.3% by SCWO treatment, but when the OE value increased to 2.0, the COD degradation rate reached 98.6%. The experimental results showed that as the temperature and OE increased, the COD degradation efficiency increased. In addition, the increase in the COD degradation efficiency was most obvious as the temperature increased from the subcritical region to the supercritical region. As the temperature increased from 673.15 to 773.15 K, the COD degradation efficiency in the liquid products continued to increase for all OE conditions. This result indicated that the main factor influencing COD degradation under these conditions was temperature. When the temperature was above 773.15 K, the increase in the COD degradation efficiency with low OE values was less than that with high OE values, which indicated that the main factor influencing COD degradation under these conditions was the OE. The maximum COD degradation efficiency of 98.6% was obtained at 823.15 K with an OE of 2, and the concentration of COD in

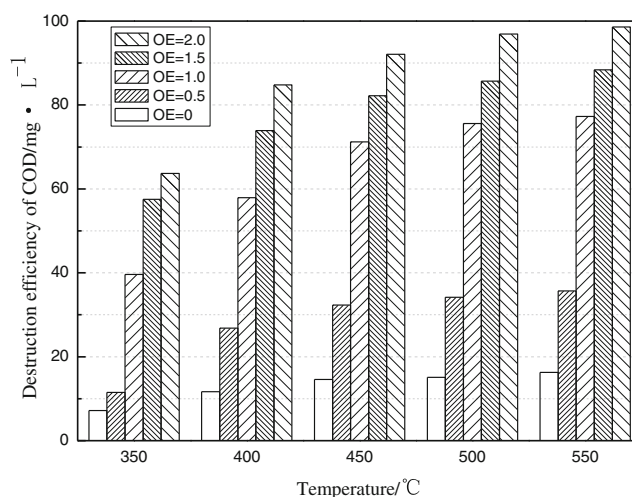


Fig. 1 The destruction efficiency of COD in liquid products under different reaction conditions

the liquid product was 605 mg/L. Relative to the initial COD concentration, the removal effect was extremely significant. Thus, substantial degradation of organic pollutants in EPS was obtained by SCWO treatment. Similarly, research by Zan et al. (2006) showed that after SCWO treatment, the COD degradation efficiency in municipal sludge reached 99.98%, and this value further increased with high temperature. Cui et al. (2009) found that COD in oily sludge could be effectively degraded by SCWO treatment, and the maximum COD degradation efficiency of 92% was obtained at 723.15 K with a 10 min SCWO treatment. Apj et al. (2018) found that 92% of COD in landfill leachate could be removed by SCWO treatment combined with ozonation at 873.15 K. Figure S2 shows a comparison of the liquid products obtained under different reaction conditions. Due to incomplete degradation of the pollutants, the liquid product obtained with low temperature and low oxidation coefficient has a dark color.

Distribution of heavy metals in products

The solubility of heavy metals in an aqueous solution is determined by the characteristics of aqueous metal complexes and their stability under particular physicochemical conditions (Hearn et al. 1969). The dielectric constant of water dramatically decreases when water is heated and pressurized above its critical point. Thus, SCW is an ideal solvent for both organic compounds and oxygen, yet inorganic materials such as heavy metals are insoluble in SCW due to the high polarity of their ions. As a result, the special characteristics of SCW force inorganic substances to convert into more stable species, reducing the mobility of heavy metals. The low solubility of salts in SCW is of great interest for scientific research and industrial applications (Michael et al. 2008; Zou et al. 2013). The high contents of the heavy metals Zn and Cr in EPS will probably be simultaneously stabilized with the degradation of organic pollutants. Thus, the Fe, Zn, and Cr concentrations in the liquid product were analyzed in this work, as shown in Fig. 2. Additionally, the distributions of Fe, Zn, and Cr in the solid and liquid products under different reaction conditions were determined, as shown in Fig. 3.

As shown in Fig. 2, the Fe, Zn, and Cr concentrations in the liquid product significantly decreased with increasing temperature and OE, indicating the positive effect of a high temperature and coefficient on Fe, Zn, and Cr precipitation. The minimum Fe, Zn, and Cr contents in the effluent were 41.7, 28.1, and 2.7 mg/L⁻¹, respectively, after treatment at 823.15 K with an OE of 2.0, which is an excellent result for high initial contents of 26.48%, 12.56%, and 4.76%, respectively. Thus, the high Fe, Zn, and Cr contents in EPS were efficiently recovered in solid ash after SCWO (Zou et al. 2013).

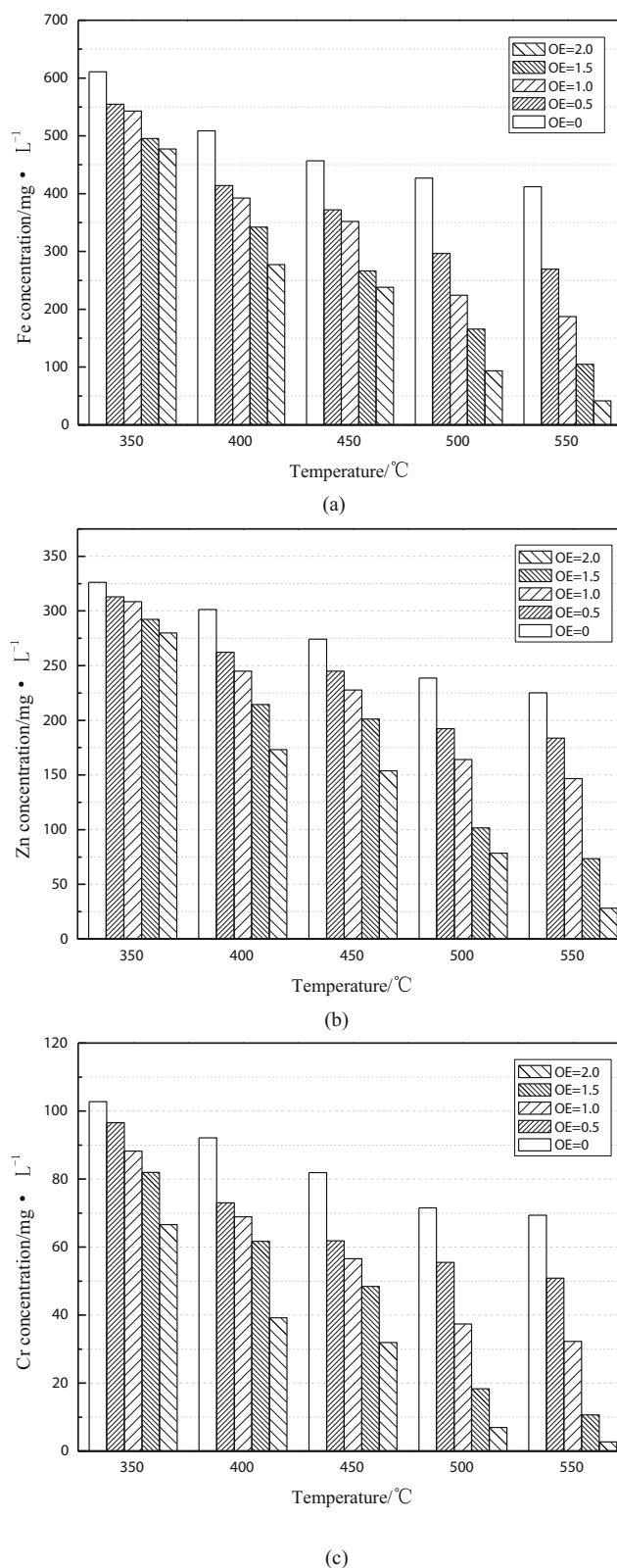


Fig. 2 The concentration of Fe (a), Zn (b), and Cr (c) in liquid products under different reaction conditions

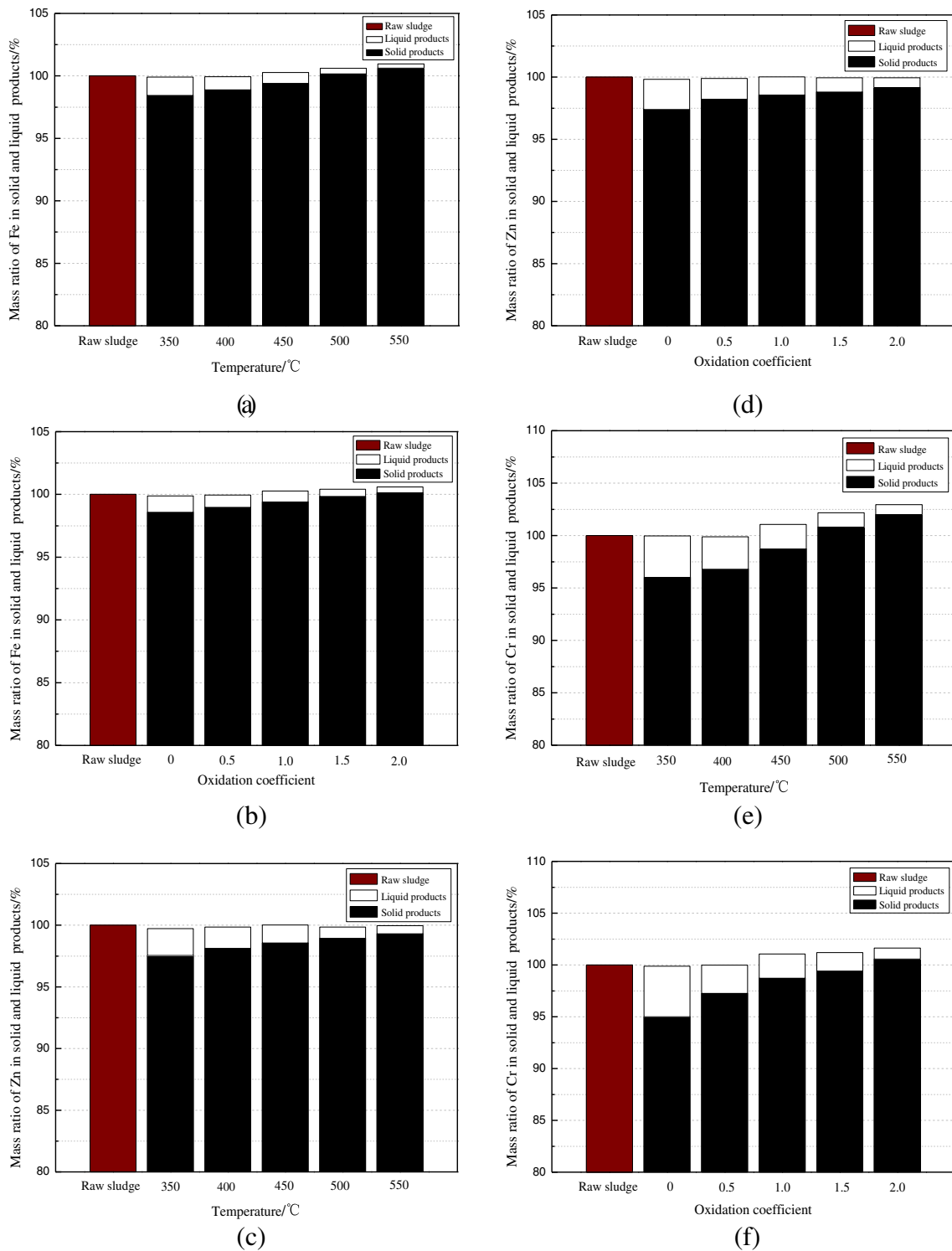


Fig. 3 The distribution proportion of Fe, Zn, and Cr in solid and liquid products under different temperatures and OE conditions

Furthermore, the distributions of Fe, Zn, and Cr in the solid and liquid products were studied. The mass ratios of Fe, Zn, and Cr in the liquid and solid products under different reaction

conditions were obtained. As shown in Fig. 3, increases in the temperature and OE promoted the transformation of Fe, Zn, and Cr into solid products. The maximum contents of Fe, Zn,

and Cr in the solid products were 100.6%, 99.2%, and 101.9%, respectively, at 823.15 K with OE of 1.0. Additional Fe and Cr were detected due to corrosion of the reactor surface (Kriksunov and Macdonald 1995; Hayward et al. 2003; Asselin et al. 2010). Less than 2% of Fe, 3% of Zn, and 6% of Cr was present in the liquid products. The transformation of Fe, Zn, and Cr into solid products was significantly promoted by the SCWO treatment. Thus, the SCWO treatment enhanced the conversion of heavy metals in EPS into solid products. Chen et al. (2016) found that Cr_2O_3 could form and separate in the treatment of industrial leather wastewater by SCWO⁶.

TCLP test of heavy metals

The TCLP standard method (US Environmental Protection Agency 1992) was used to determine the leaching toxicity of the heavy metals in the solid products. The TCLP results for the raw sludge are presented in Table S2. The amounts of Zn and Cr leached reached 147 mg/L and 21 mg/L, respectively, which greatly exceed the permitted limits of the US EPA and Chinese EPA (Ministry of Environmental Protection of China 1997), meaning that the ashes are hazardous waste. After the EPS was treated with SCWO, the leaching toxicity of the heavy metals in the solid products significantly decreased compared with the raw sludge.

The results in Table S3 show that the leachate of the solid products surpassed the permitted limits of the US EPA and Chinese EPA standards in SCW at 623.15 K. However, the leaching toxicity of Zn was below the above standards when the temperature of the SCWO treatment exceeded 673.15 K. The leaching toxicity of Cr was 2.1 mg/L and 3.2 mg/L when the temperature was above 773.15 K or the OE was above 1.5, respectively, indicating that the leaching toxicity is reduced to a safe level. The minimum leaching toxicity of Zn and Cr was 15.8 mg/L and 0.4 mg/L, respectively, for treatment at 823.15 K. The heavy metal concentrations of the liquid products decreased at low temperature (623.15 to 723.15 K) and OE (0 to 1) conditions due to the heavy metals combining with unstable compounds or adsorbing on certain substances and transferring to the solid products. Thus, a higher leaching toxicity of heavy metals was detected in these solid products. Similarly, Chen et al. (2017) observed that the heavy metals in lignite transformed from unstable to stable with increasing temperature in a SCW gasification treatment process. Additionally, the carbonate and oxide forms of heavy metals can form to improve the stability of heavy metals in deinking solid residue (Zhen et al. 2000). To compare the transfer and stabilization of Zn and Cr in the solid and liquid products under different experimental conditions, the ratio of the leaching toxicity

of Zn and Cr in solid products to that of the raw sludge and the ratio of the Zn and Cr in the liquid products to the total mass were investigated. The value of Y_1 indicates the ratio of the leaching toxicity of Zn and Cr in the solid products under different SCWO conditions to that of the raw sludge, L is the leaching toxicity of Zn and Cr in the solid products, L represents the leaching toxicity of Zn and Cr in the raw sludge, i represents Zn and Cr, and j represents the different SCWO conditions, as indicated by Eq. (1).

$$Y_1 = \frac{L_{ij}}{L} \quad (1)$$

Here, the value of Y_2 demonstrates the mass ratio of Zn and Cr in the liquid products, S is the mass of Zn and Cr in the solid products, L represents the mass of Zn and Cr in the liquid products, i represents Zn and Cr, and j represents the different SCWO conditions, as indicated by Eq. (2).

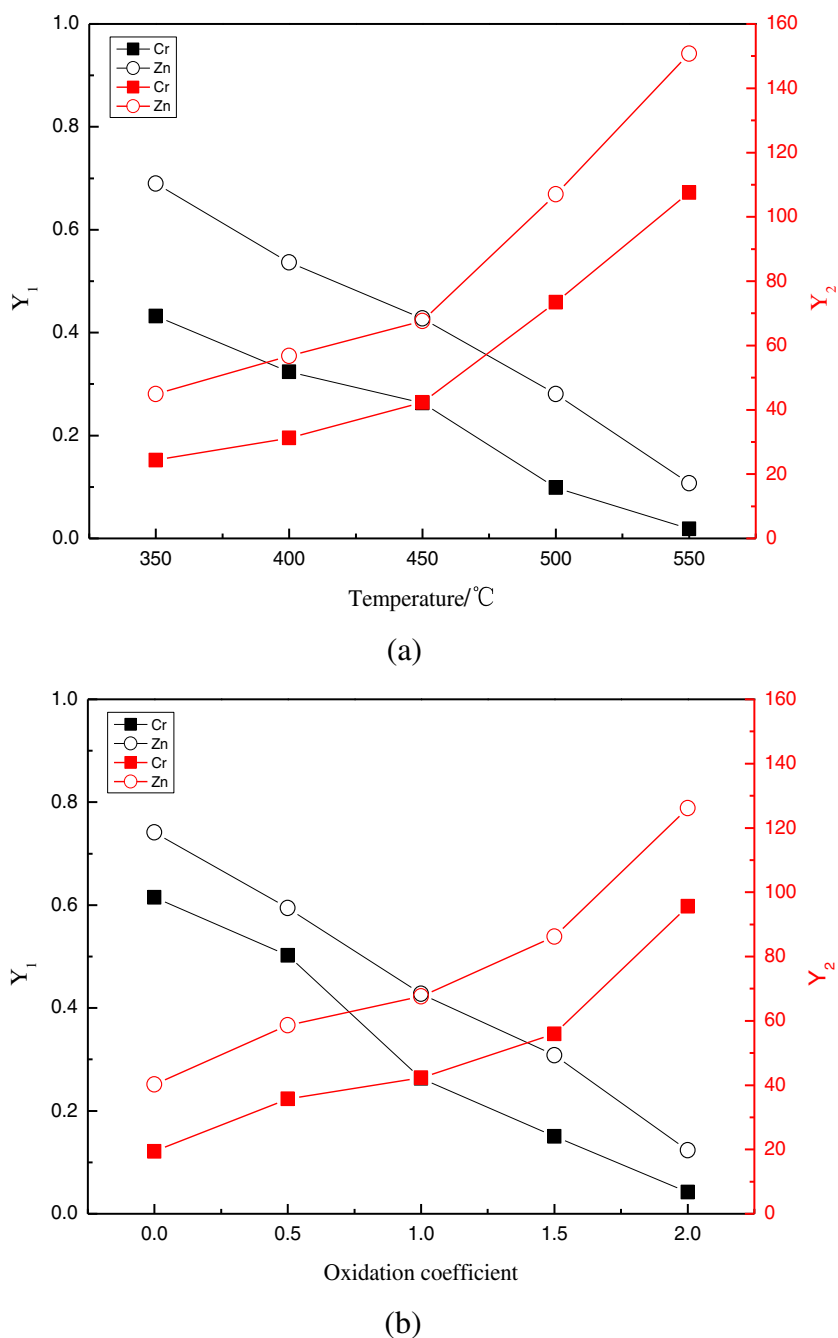
$$Y_2 = \frac{S_{ij}}{L_{ij}} \quad (2)$$

The values of Y_1 and Y_2 are shown in Fig. 4. A comparison of the leaching toxicity of the solid products and the Zn and Cr contents in the solid and liquid products shows that the proportion of Zn in the liquid products was less than that of Cr, but the leaching toxicity of Cr was significantly less than that of Zn. The leaching toxicity of the heavy metals in the solid products was used as the standard to evaluate the degree of stabilization. Cr was more stable than Zn in the EPS after SCWO treatment under the same conditions. Compared with Cr, Zn could more easily transform into solid products, but Zn was also more easily leached from the solid products. The reason for this result may be that Cr_2O_3 crystals have the same structure as $\alpha\text{-Al}_2\text{O}_3$, which inhibits reactions with hydrogen ions. Therefore, Cr_2O_3 is more difficult to dissolve in acids than ZnO and is more stable (Sun et al. 2006; Sato and Akimoto 2008).

Analysis of the solid phase products

It is necessary to analyze the solid products to further understand the conversion behavior of heavy metals and the effect of Fe on the transformation of Zn and Cr in the SCWO treatment process. The solid phase product analysis in this study was divided into two parts: morphology and composition. First, a SEM analysis was performed on the raw sludge and the solid products obtained after treatment at 823.15 K, as shown in Fig. 5. A

Fig. 4 The comparison of leaching toxicity and content in liquid products of Zn and Cr under different temperatures (a) and OE (b)



comparison shows that the of the solid products from SCWO treatment at 823.15 K obviously have a porous morphology due to the degradation and dissolution of organic pollutants and the transformation of heavy metals. In contrast, the raw sludge has a more compact appearance. In addition, crystals were observed in the solid products, indicating that crystallization occurred during the SCWO treatment. Additionally, an XRD analysis was performed on the raw sludge and solid products.

As shown in the XRD patterns (Fig. 6), Fe₃O₄, ZnO, ZnFe₂O₄, and FeCr₂O₄ were present in the solid products,

but these species were not detected in the raw sludge. The EPMA was calibrated with metal oxide standards to obtain quantitative concentration data. The calibration procedure is discussed in the references (Zhen et al. 2000; Zheng and Koziński 2000).

The EPMA analysis results are shown in Table S4. Fe₃O₄ resulted in the presence of Fe₃O₄, ZnFe₂O₄, and FeCr₂O₄. ZnO resulted in ZnO and ZnFe₂O₄. Cr₂O₃ came from FeCr₂O₄. As shown in Table S3, the increase in the temperature and OE promoted the formation of Fe, Zn, and Cr oxides in the solid products. The maximum mass ratio of Fe and Cr

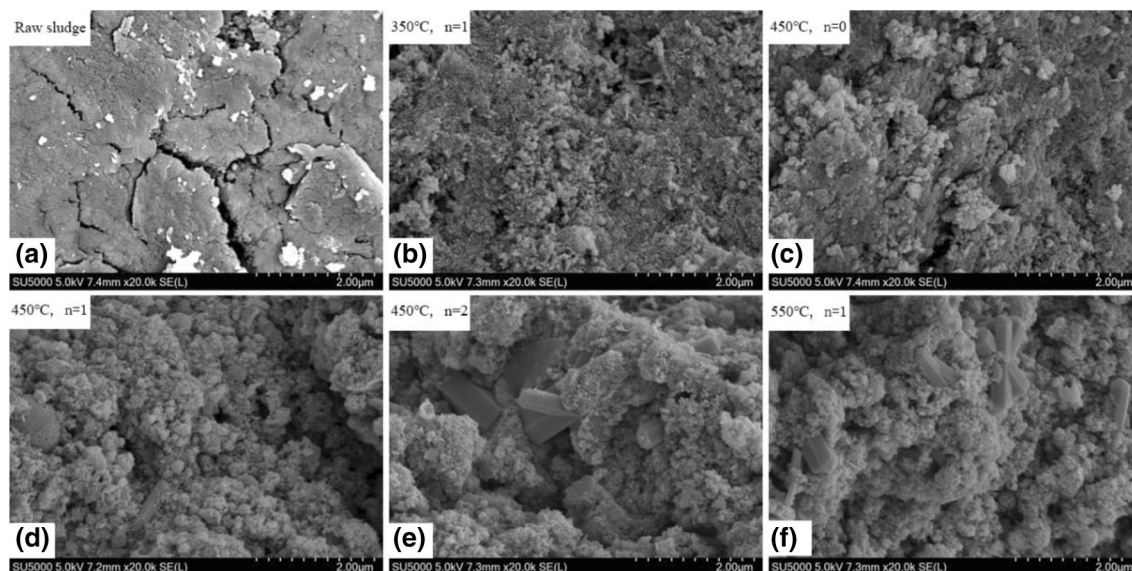


Fig. 5 SEM images of (a) raw sludge, (b) solid product of 623.15 K, OE = 1 treatment, (c) solid product of 723.15 K, OE = 0 treatment, (d) solid product of 723.15 K, OE = 1 treatment, (e) solid product of 723.15 K, OE = 2 treatment, and (f) solid product of 823.15 K, OE = 1 treatment

oxides was 61.38% and 4.52%, respectively, in the solid products treated by SCWO at 823.15 K with OE 1. However, the maximum mass ratio of Zn was 18.27% with SCWO treatment at 723.15 K with OE 2. These results indicated that Fe, Zn, and Cr have a tendency to convert to oxides during SCWO treatment and exist in a more stable state. As a result, the leaching toxicity of Fe, Zn, and Cr from the solid products obtained at high temperature and OE was lower. Combined with the XRD analysis results, this study shows that Fe-Zn and Fe-Cr systems can be formed by SCWO treatment to stabilize Fe, Zn, and Cr in solid products. It was verified that Fe plays a positive role in the stabilization of Zn and Cr by forming spinel compounds during SCWO treatment. Researchers have found that spinel compounds with relatively stable properties can be formed by Fe oxides with Zn

and Cr oxides at high temperature and pressure (Figuerola and Stewart 2008; Andersson and Stanek 2013).

Stabilization mechanism of Zn and Cr

Heavy metals entering a SCWO system were oxidized and formed stable compounds because of dissolution or decomposition of adsorbents and decomposition or transformation of unstable heavy metal compounds (Zhen et al. 2000). Due to the high iron content in sludge, Fe-Zn and Fe-Cr systems formed through chemical combination of Fe, Zn, Cr, and O_2 in SCW, making Zn and Cr more stable. At the same time, stable oxides of Fe, Zn, and Cr formed with O_2 . As shown in Fig. 7, some Fe combined with Zn, Cr, and O_2 to form $ZnFe_2O_4$ and $FeCr_2O_4$, and some Fe combined with O_2 to form Fe_2O_3 . Some of the Zn was oxidized to ZnO. Almost all of the Cr was converted to $FeCr_2O_4$ because of its low content. These results are consistent with Langton's (1989) findings that heavy metals can be stabilized as crystals through nucleation and deposition. Additional Fe and Cr entered the SCWO reaction system because of corrosion of the inner surface of the reactor. Fe, Zn, and Cr were transformed from free, adsorption, and unstable compounds to stable compounds by SCWO treatment.

In a similar study, Chen et al. (2017) found that Zn and Cr in lignite can be transformed from the F3 and F4 fractions to the F5 fraction, which reduced the leaching toxicity of Zn and Cr during SCW treatment²². In summary, Zn and Cr in an EPS solution undergo a long heating process and complex transformation with Fe and O_2 to form oxides. Therefore, Zn and Cr stabilization might be attributed to the formation of oxides that reduce Zn and Cr bioavailability and mobility in the environment.

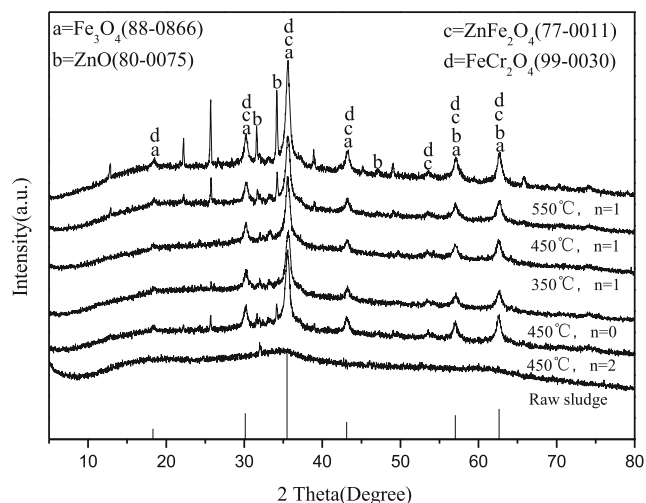


Fig. 6 XRD spectra of solid products from different experimental conditions. Images (a) Fe_3O_4 , (b) ZnO, (c) $ZnFe_2O_4$, and (d) $FeCr_2O_4$

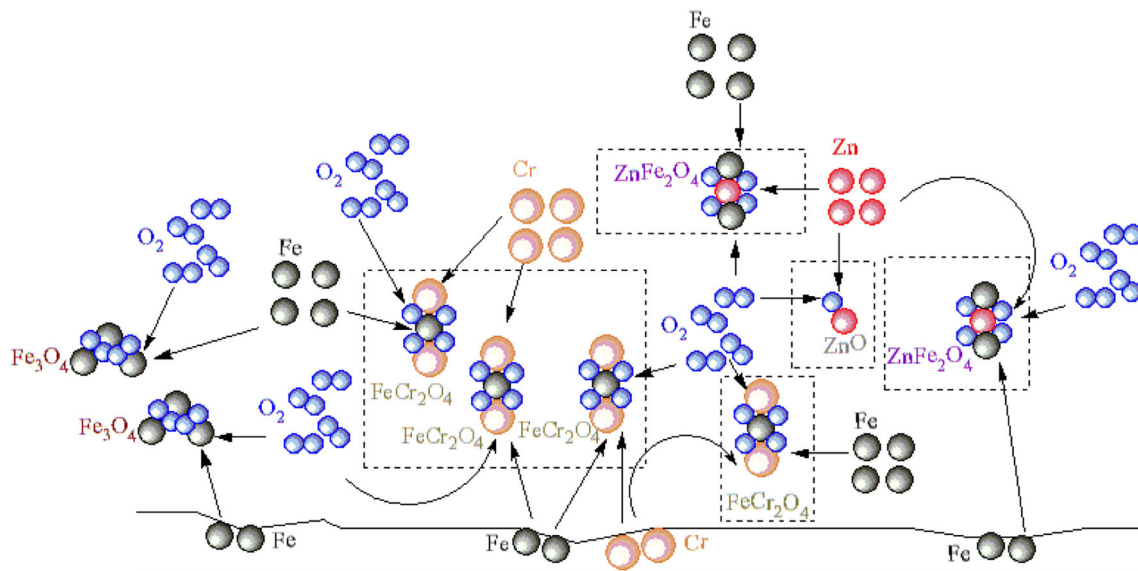


Fig. 7 Transformation of Fe, Zn, and Cr in 823.15 K SCWO treatment

Conclusions

The results of this study prove that SCWO is an effective process for treating EPS. Both organic pollutants and high Zn and Cr contents could be simultaneously removed. Additionally, heavy metals such as Zn and Cr in solid products were stabilized and had minimal leaching toxicity, making the residue environmentally friendly. The maximum COD removal efficiency, which was mainly promoted by high temperature and OE, was 98.6% at 823.15 K, OE of 2, reaction time of 7 min and reaction pressure of 25 MPa. Less than 2% of Fe, 3% of Zn, and 6% of Cr were present in the liquid products under these conditions. The transformation of Fe, Zn, and Cr into solid products was significantly promoted by SCWO treatment. Heavy metals migrated to solid products and transformed from an unstable form to a stable form during the SCWO process. The leaching toxicity of Zn and Cr in the solid products was significantly reduced to meet the US EPA and Chinese EPA limits after SCWO treatment. A comparison shows that the Zn in EPS is more easily converted into a solid product after the SCWO treatment, but Cr is more difficult to leach from the solid product. According to the SEM, XRD, and EPMA results, Zn and Cr in EPS are transformed from unstable forms to stable oxides (ZnO , ZnFe_2O_4 , and FeCr_2O_4) after SCWO treatment, indicating that Fe plays a positive role in the stabilization of Zn and Cr. This result explains why the leaching toxicity of Zn and Cr in the solid products was significantly reduced compared with that of the raw sludge. Stabilization of Zn and Cr in EPS could be implemented during SCWO treatment.

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