Contents lists available at ScienceDirect

Process Safety and Environmental Protection

journal homepage: www.elsevier.com/locate/psep

Preparation of a metal-phosphate/chromium oxide nanocomposite from Cr(III)-containing electroplating sludge and its optical properties as a nanopigment

Yang Li[a], *Hua Zhang*[a,*], *Li-Ming Shao*[b,c], *Pin-Jing He*[b,c,*]

[a] *State Key Laboratory of Pollution Control and Resources Reuse, Tongji University, 1239 Siping Road, Shanghai 200092, PR China*

[b] *Institute of Waste Treatment and Reclamation, Tongji University, 1239 Siping Road, Shanghai 200092, PR China*

[c] *Research and Training Center on Rural Waste Management, Ministry of Housing and Urban-Rural Development of PR China, 1239 Siping Road, Shanghai 200092, PR China*

ARTICLE INFO

Article history:
Received 11 April 2015
Received in revised form 5 August 2015
Accepted 10 August 2015
Available online 20 August 2015

Keywords:
Electroplating sludge
Resource recovery
Chromium oxide
Nanocomposite
Nanopigment
Optical performance

ABSTRACT

A nanocomposite composed of metal-phosphates and chromium oxide was prepared from a Cr(III)-containing electroplating sludge (CES) by a facile three-step (extraction–precipitation–calcination) process. Optimal process parameters were determined, and the structure of the metal-phosphate/chromium oxide nanocomposite (MPCON) was investigated by field-emission scanning electron microscopy, Fourier transform infrared spectroscopy, X-ray diffraction, and X-ray photoelectron spectroscopy. The results show that the optimal extraction pH is 2.0. The MPCON presents a polyhedral morphology with average particle size of around 100 nm. The components of MPCON vary from $AlPO_4/Cr_2O_3$ to $Mg_3(PO_4)_2/AlPO_4/Cr_2O_3$ at different solution pH during precipitation. Meanwhile, the optical performance of the nanocomposite as a pigment is discussed. The reflectance of MPCON-6.5 in the near-infrared range is around 56%, making it a strong prospect to be used as a functional pigment in energy-efficient buildings. This study proposes a novel recycling process for the conversion of CES into high-value products, which is beneficial for the treatment of waste.

1. Introduction

The chromium electroplating process, which is broadly applied in metal surface treatment to improve surface properties, such as smoothness and durability, produced considerable amounts of Cr(VI) wastewater. For chromium wastewater treatment, the adsorption is the most popular method due to high removal efficiency (Qiu et al., 2014, 2015; Zhu et al., 2012). Considering that Cr(VI) is more toxic than Cr(III) in the electroplating industry, the method, the reduction of Cr(VI) to Cr(III) and precipitation of Cr(III), has been applied to treat Cr(VI) electroplating wastewater. However, Cr(III)-containing electroplating sludge (CES) are generated from treatment method (Odle et al., 1991). CES is classified as hazardous waste because of leaching toxicity. Thus, further treatment and disposal of CES is necessary. Although stabilization/solidification has become a widely accepted treatment option for CES by immobilizing chromium and other heavy metals, it is unfavorable because it occupies too much hazardous waste landfill capacity and allows for minimal resource recovery (Asavapisit and Chotklang, 2004).

* *Corresponding author.* Tel.: +86 21 65986104; fax: +86 21 65986104.
E-mail addresses: sqqsli@126.com (Y. Li), zhanghua_tj@tongji.edu.cn (H. Zhang), solidwaste@tongji.edu.cn (P.-J. He).
http://dx.doi.org/10.1016/j.psep.2015.08.005
0957-5820/

Table 1 – Elemental composition (dry-weight percent) of the Cr(III)-containing electroplating sludge.

Element	Na (%)	Mg (%)	Al (%)	Si (%)	P (%)	Cl (%)	Ca (%)	Cr (%)
Content	0.53	1.52	1.08	3.43	3.05	1.15	13.8	9.77
Element	Zn (%)	Mn (%)	Fe (%)	C (%)	H (%)	S (%)	N (%)	
Content	0.33	0.61	1.42	5.56	1.60	3.87	0.71	

CES resource reuse has been applied in the production of green pigment and ceramic materials (Andreola et al., 2008; Perez et al., 1996). For example, Li et al. (2014a,b) report that CES could be used as a green pigment in cement-based decorative mortar. However, some disadvantages, including excessive impurities, uncontrollable crystal structure, and Cr(VI) formation during high-temperature processes, reduce the value of the obtained products. To obtain high value-added products, current research efforts focus on converting Cr-containing waste into advanced multifunctional nanostructured materials (Ashokkumar et al., 2013; Rao et al., 2002). One step or multi-step treatments have been employed, including extraction of Cr from Cr-containing waste and synthesis of Cr-based nanomaterials (Kido et al., 2014; Silva et al., 2005). Chrome-tanned leather was utilized to produce a chromium-carbon core-shell nanomaterial via thermal treatment, and the nanomaterial was used for catalysis in an aza-Michael addition reaction as well as electromagnetic interference shielding applications (Ashokkumar et al., 2013).

In recent decades, studies on nanostructural chromium oxide have become a hot area mainly because of its outstanding properties, for example, increasing pigment opacity and enhancing catalytic activity. Compared to single-component Cr_2O_3, nanocomposite structures can control optical, catalytic and electrochemical performance depending on the requirement. So far, various Cr_2O_3-based nanocomposites, such as Cr_2O_3—$3TiO_2$, C—Cr_2O_3, Cr_2O_3/12-phosphotungstic acid, and $CoFe_2O_4$—Cr_2O_3—SiO_2, have been prepared and applied as pigments and catalysts (Borgohain et al., 2010; Fu et al., 2015; Jiang et al., 2010; Tamiolakis et al., 2012). Metal phosphates are also profusely investigated for many advanced applications, such as pigment, catalysts, and electrochemistry (Sarkar and Mitra, 2014; Souiwa et al., 2015). Considering that there are large amounts of P and other metals besides Cr in the CES, the recovery of Cr_2O_3 and metal phosphates from CES and the production of metal-phosphate/chromium oxide nanocomposites (MPCON) with high value were investigated.

A traditional one-step thermal treatment process cannot successfully synthesize this nanocomposite due to the uncontrollable nature of the crystal structure. Herein, this study presents a three-step method (extraction–precipitation–calcination) to prepare a MPCON. The optimal process parameters were studied, and the structure, composition, and morphology of the nanomaterial under different pH conditions were characterized. In addition, the optical properties of MPCON as a pigment are discussed.

2. Experimental

2.1. Materials

All chemical reagents were analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd., China. CES was collected from a Cr(VI) electroplating wastewater treatment (reduction and precipitation) unit located in steel rolling mills of a steel plant. The raw CES was dried in an oven at 105 °C for 24 h and ground to a particle size <150 μm. The elemental composition of the CES is shown in Table 1, and was analyzed using an X-ray fluorescence spectrometer (XRF) and a CHNS elemental analyzer. The CES contains 13.8 wt% Ca, 10.9 wt% Cr, 3.89 wt% Si, 3.05 wt% P, 1.58 wt% Mg and 1.18 wt% Al. The X-ray diffraction (XRD) pattern of CES is dominated by peaks arising from $CaCO_3$ and $CaSO_4$ (Fig. 1).

2.2. Extraction experiment

Mixtures of different concentrations of HNO_3 and 0.53 M $(NH_4)_2SO_4$ were used to extract Cr from CES. $(NH_4)_2SO_4$ was added to reduce the Ca concentration in the extract. 10 g of CES were mixed with 100 mL of the mixed extraction solution in a 250 mL flask with a lid to achieve a final pH (pH_f) of 1.0–7.2 and a Ca/S molar ratio of 1.0:1.5. After shaking at 25 °C for 1 h in a shaking incubator, the mixture was filtered through a 0.45-μm microporous membrane to remove the residue. The mineral composition of the residue was examined by XRD with a Cu Kα X-ray radiation source (λ = 0.154 nm) at a scanning rate of 0.1 s/step from 10° to 70°. The elemental concentrations in the filtrate were measured by an inductively coupled plasma optical emission spectrometer (ICP-OES).

2.3. Synthesis of MPCON

In a 150 mL flask, 10 mL of the above-mentioned filtrate was mixed with a specified amount of the surfactant

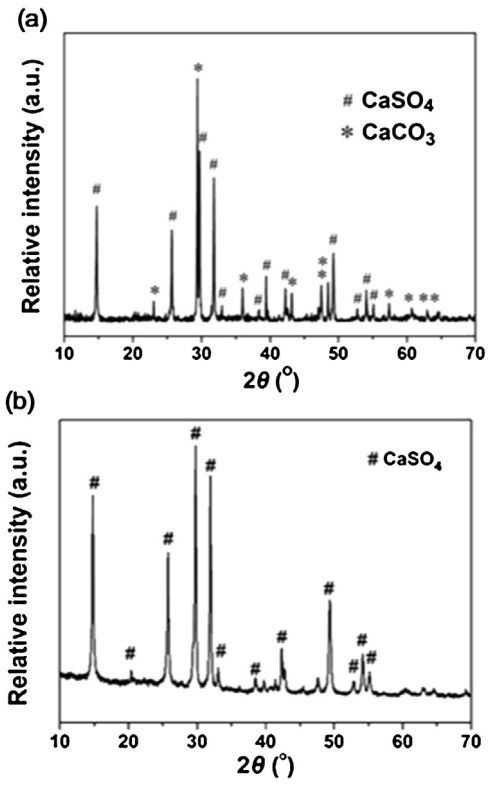

Fig. 1 – XRD pattern of (a) CES and (b) the residue after extraction.