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Chromium (VI) and zinc (II) waste water co-treatment by forming layered double hydroxides: Mechanism discussion via two different processes and application in real plating water

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ABSTRACT

Two processes, adsorption after synthesis (AAS) and adsorption during synthesis (ADS) were compared in CrO_4^{2-} and Zn^{2+}/CrO_4^{2-} removal. Kinetic results showed that ADS was a better method than AAS, since Cr content was 0.65/0.81 mmol/g in Cr-ADS/ZnCr-ADS, but it was only 0.37/0.56 mmol/g in Cr-AAS/ZnCr-AAS. Then, a low-cost mixture was proposed to function as ADS raw materials in treating real plating waters. This mixture first got an isothermal saturation of 1.1 mmol/g in simulated CrO_4^{2-} water. When Zn^{2+} was co-treated, it was increased to 1.3 mmol/g. At the same time, a Zn^{2+} removal of 1.5 mmol/g was attained. Furthermore, real plating water co-treatment reached equilibrium in 6 h and obtained 1.4/0.9 mmol/g for Zn^{2+}/CrO_4^{2-}, respectively. According to XRD analysis, this co-treatment enhancement resulted from the formation of Zn and Cr contained layered double hydroxide.

1. Introduction

Metal-plating industry created large volumes of wastewater containing toxic metal ions such as Cd, Cu, Pb, Ni, Cr, and Zn ions [1,2]. All these substances are highly toxic and have been regulated by countries worldwide. Among them, CrO_4^{2-} and Zn^{2+} are typical anionic and cationic. CrO_4^{2-} is a highly hazardous material, being a mutagen and a potential carcinogen [3,4]. Greatly extra amount of Zn^{2+} in the environment may be very harmful because of its possibility of leading to irritability, lung disorders and even cancer [5]. Therefore, CrO_4^{2-} and Zn^{2+} effluents must be properly treated so as not to cause more damage to the environment. Recently, adsorption of CrO_4^{2-} or Zn^{2+} with a suitable adsorbent is widely studied [6–8]. However, since CrO_4^{2-} and Zn^{2+} were anionic and cationic, respectively, their co-treatment was seldom investigated.

Many adsorbents have been developed and studied on the adsorption characteristics towards specific contaminants. For example, CrO_4^{2-} can be adsorbed on materials, such as active carbons, anion exchange resins, natural fibers, biomass, various inorganic materials and inorganic nanoparticles [9–12]. Several kinds of environmental friendly materials have been observed to have high adsorption capacity for Zn^{2+} [13–15]. Among these choices, active carbons and anion exchange resins always result well CrO_4^{2-} removal efficiency. However, the production of active carbon is usually high energy cost (generally > 600 °C) [9]. Anion exchange resins are also costly in production. Other natural fibers and biomass are easily obtained but usually only have relative low removal amounts on CrO_4^{2-}. Compared with these methods, layered double hydroxides materials can be synthesized by low cost materials. Furthermore, they can take up CrO_4^{2-} in the interlayer with strong electrostatic interactions, showing a better adsorption property for CrO_4^{2-} removal [12,16,17]. Although layered double hydroxide is anion exchange clay and not usually researched on cation pollution removal, such as Zn^{2+}. However, Zn^{2+} is an ordinary component of layered double hydroxides [18,19], ordinarily but significantly, promising a possibility of Zn^{2+} and CrO_4^{2-} co-treatment.

Layered double hydroxides (LDHs) are a family of anionic clay materials. They can chemically be expressed as a general formula of $[M_{1-x}^{2+}M_x^{3+}(OH)_2](A^{n-})_{x/n}\cdot yH_2O$ [20–22], where M^{2+} and M^{3+} are any divalent (for example Zn^{2+}) and trivalent cations. A^{n-} is an exchangeable interlayer anion (for example CrO_4^{2-}). The most important property of LDHs is the high anion exchange capacity, promising the high removal efficiency of anionic contaminants [23–25]. As a matter of fact, LDHs have been noted to adsorb CrO_4^{2-} in a reasonably high amount both in batch and column experiments [16,26]. It is our hypothesis that merging CrO_4^{2-} and Zn^{2+} treatment is possible and applicable.

Therefore, this work is aimed to prove the possibility and applicability of CrO_4^{2-}/Zn^{2+} co-treatment via layered double hydroxides both in simulated and real waste water. To this end, we first

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compared CrO_4^{2-} and Zn^{2+} adsorption by two different methods. (1) adsorption after synthesis (AAS); (2) adsorption during synthesis (ADS). Kinetic and isothermal adsorptions were carefully finished and mechanisms were investigated. Then, according to these results, a novel method via batch experiments was proposed to treat real CrO_4^{2-} and Zn^{2+} plating water.

2. Experimental

2.1. Adsorption after the synthesis of LDHs

CaAl-Cl LDHs (Friedel's salt) was prepared by a coprecipitation method, as described elsewhere [27]. In general, two solutions were first prepared, one contained 1 mol/L $CaCl_2$ and 0.5 mol/L $AlCl_3$, and another one contained 1.5 mol/L NaOH. Then they were mixed at a volume ratio of 1:2 under vigorous stirring with a magnetic stirrer. The synthesis of Friedel' salt was performed under nitrogen protection in order to prevent the probable influence of CO_2. All reagents were of reagent grade quality and were purchased from Sinopharm Chemical Reagent Co. Ltd. After aging overnight at room temperature, the resultant slurry was collected and washed by distilled water during filtration. Finally, it was dried at 105 °C for 24 h. The obtained sample was ground and stored in a desiccator for further use.

Formula of this synthesized Friedel's salt was then analyzed as $Ca_{3.8}Al_2(OH)_{11.6}Cl_2(H_2O)_{5.8}$ by inductively coupled plasma optical emission spectrometer (ICP-AES). In the end, 0.2 g of this solid was used to adsorb 50 ml of 10 mmol/L CrO_4^{2-} or 28.5 mmol/L Zn^{2+} + 10 mmol/L CrO_4^{2-} contaminated water. We call this process as adsorption after the synthesis of LDHs (defined simply as AAS).

2.2. Adsorption during the synthesis of LDHs

In the former AAS method, if 0.2 g input of Friedel's salt were totally dissolved in the targeted 50 ml waste water, concentrations of Ca^{2+}, Al^{3+} and OH^- would be about 28.5, 14.3 and 85.5 mmol/L, respectively. According to these, two solutions were mixed to create a process of LDHs synthesis and pollution adsorption at the same time. They were one salt solution containing 57 mmol/L Ca^{2+} and 28.5 mmol/L Al^{3+}, another CrO_4^{2-} contaminated water with 171 mmol/L NaOH. When Zn^{2+} was co-treated, 57 mmol/L Zn^{2+} would be added in the former salt solution. 25 ml liquid from each solution were then mixed together for LDHs synthesis and ions adsorption. We call this process as adsorption during the synthesis of LDHs (distinctly defined as ADS).

2.3. Application of adsorption during the synthesis

After all, input of pure reagent is not as economic as low cost materials, such as cement. Considering real application, cement was utilized to replace salt solution, since it could function as a source of Al. It was identified that the cement used in our work contained about 50% Al_2O_3. As a result, cement and $Ca(OH)_2$ were mixed thoroughly with a weight ratio of 45:31 to create a Ca/Al mole ratio of about 2. The resulted mixture was kept for further application of adsorption during the synthesis to treat real Zn^{2+} (20 mmol/L)/CrO_4^{2-} (14 mmol/L) plating water.

2.4. Characterization

Ca^{2+}, Al^{3+}, Zn^{2+} and CrO_4^{2-} concentrations before and after adsorption in all experiments were determined by inductively coupled plasma optical emission spectrometer (ICP-AES). The evolved solids were washed by distilled water after filtration. They were dried at 100 °C for further components and XRD analysis. Components analysis was applied to determine the exact metal ratio in dried solids. In general, 0.05 g was dissolved in diluted acid before concentrations being detected by ICP-AES. Chloride in solutions was titrated with silver nitrate. The XRD patterns of all obtained compounds were recorded in an XRD DLMAX-2550 (Rigaku Co.) using Cu K_α radiation (λ = 0.15418 nm) from 5 to 80° at a scanning rate of 8°/min.

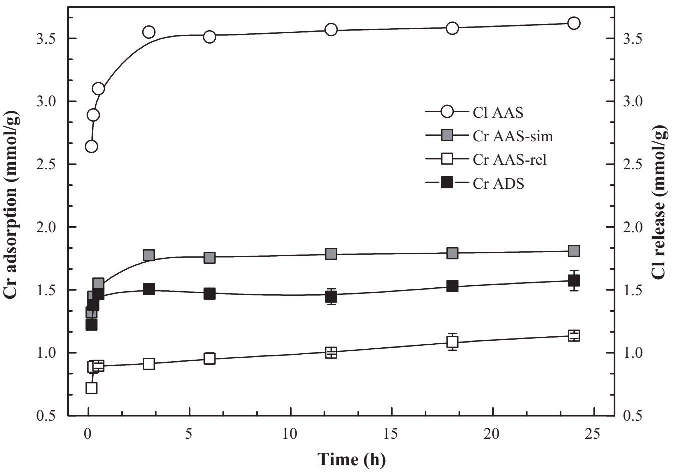

Fig. 1. Cr(VI) removal by adsorption after synthesis (AAS) and adsorption during synthesis (ADS); Cr AAS-rel is the real Cr(VI) adsorption data. Cr AAS-sim is theoretical Cr(VI) adsorption amount according to chlorine release.

3. Results and discussion

3.1. CrO_4^{2-} removal by AAS and ADS

Fig. 1 compares adsorption after synthesis (AAS) with adsorption during synthesis (ADS) on removal process. It is obvious that ADS obtained a better removal effect than AAS, since the former reached an adsorption amount of 1.5 mmol/g, while the latter only got a 1.1 mmol/g. However, they were neither bigger than the theoretical 1.8 mmol/g according to the adsorbent weight. Still, both methods attained equilibrium at about 3 h.

In the AAS method, Cl^- released from Friedel's salt into solution step by step and maintained at about 3.6 mmol/g after 3 h. Similarly, the CrO_4^{2-} removal got equilibrium at the same time, exhibiting a possible anion exchange process. In addition, CrO_4^{2-} has a higher inclination into the LDH interlayer than Cl^- [28]. In this work, it was likely that most of Cl^- was exchanged by other anions, such as CrO_4^{2-}, since there was theoretically 3.6 mmol/g Cl^- in the Friedel's salt according to the synthesized formula. If Cl^- was totally exchanged by CrO_4^{2-}, CrO_4^{2-} removal amount would be half of Cl^- release amount, which was also depicted in Fig. 1(Cr AAS-sim). It was clear that Cr AAS-rel was lower than Cr AAS-sim for about 1 mmol/g. There were two main reasons. Firstly, other anions (CO_3^{2-}, HCO_3^-, etc.) probably entered into the interlayer [28]. Secondly, part of Friedel's salt dissolved into the solution. As a result, the real amount was much smaller, and AAS method got a final removal of 1.1 mmol/g.

As for ADS method, Cl^- was kept at almost 0.11 mol/L during the whole process. Since Cl^- was 0.21 mol/L in the origin Ca^{2+} and Al^{3+} solution by titration, the total Cl^- input would be 0.11 mol/L after the mixture of Ca^{2+}/Al^{3+} and NaOH solutions. Considering this, Cl^- seemed to play no role in exchanging CrO_4^{2-} in ADS. On the other hand, CrO_4^{2-} removal amount reached balance at 1.5 mmol/g within the first 0.5 h, faster than AAS method which attained balance at about 3 h. Although it was still a little lower than the theoretical 1.8 mmol/g, it was much bigger than the 1.1 mmol/g