

Optimum pHs for Cr(VI) co-removal with nucleated Cu(II) precipitation in continuous-flow fluidised metal strippers

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Abstract

A compact nucleated precipitation technology using two fluidised sand columns in series was developed to pretreat model metal-plating wastewater containing high concentrations of Cu(II) and Cr(VI). Since either Cu(II) precipitation or Cr(VI) co-removal with Cu(II) precipitation was found to be highly pH dependent in batch tests, the continuous-flow studies were conducted under different pHs. Experimental results show that high pH has no positive influence on either Cr(VI) or Cu(II) removal in the continuous-flow fluidised metal stripper technology. Operation at pH 6.5 in both columns can obtain significantly higher levels of both total Cr(VI) and total Cu(II) removal compared with work at pH 9.5 in both columns and work at pH 6.5 and 9.5 in the 1st and 2nd columns, respectively.

Keywords: nucleated precipitation, continuous-flow fluidised metal stripper, Cr(VI), Cu(II)

Introduction

Many industries, including electroplating, printed circuit, metal finishing, tanneries, photographic, and dye manufacturing, etc., generate wastewater containing variable levels of Cr(VI). Although selective ion-exchange (Segupta, 1986), membrane technology (Ho and Poddar, 2001; Ghosh et al., 2006; Hafez and Manharawy, 2004), adsorption by natural and modified adsorbents (Prasad and Freitas, 2000; Malkoc and Nuhoglu, 2006; Celis et al., 2000; Gode and Pehlivan, 2006), etc., have been successfully demonstrated at laboratory-scale level, they have not been employed in full-scale operation because of high operation costs and generation of pollution. Removal of Cr(VI) by bacterial strain and fungal strain (Shrivastava and Thakur, 2003; Srivastava and Shekhar, 2006) have been investigated in recent years. However, the lower removal efficiency and longer time requirement limit their practical use. Chemical reactions involving reduction of Cr(VI) to Cr(III) by different reducing agents such as NaHSO₃, FeS, FeSO₄, SO₂, etc., followed by a hydroxide precipitation of Cr(III) (Erdem et al., 2001) have received great attention and were found to operate effectively with higher rate and higher recovery. They are the most widely used methods in full-scale operation over the past decades, especially for high-load (either volume or mass) wastewater streams. However, the methods are restricted due to the cost of the chemicals used and the quality and amount of the sludge produced. Finding cost-effective and space-saving methods for Cr(VI) elimination suitable for practical use and large-scale operation are attractive and important work.

On the basis of heterogeneous precipitation, a single-step compact method was developed by Huang and co-workers to remove such heavy metals as Cu(II), Ni(II), and Zn(II) from

industrial wastewaters, including electroplating, printed circuit and metal finishing, etc. The new method uses a fluidised sand column to serve as a metal stripper. Unexpectedly, a large amount of aqueous Cr(VI) was co-removed from the plating wastewater containing Cu(II), Ni(II), Zn(II), and Cr(VI) under an operation at pH 9.5 (Zhou et al., 1999).

Cr(VI) exists mainly in soluble forms of HCrO₄⁻, Cr₂O₇²⁻ and CrO₄²⁻ in the aqueous environment. They cannot form any precipitate in reaction with either CO₃²⁻ or OH⁻ ions, unless they are first reduced to Cr(III). Therefore, the mechanisms involved in co-removal of Cr(VI) with the precipitation of other heavy metals were further examined through a series of batch studies. Co-precipitation involving the formation of copper-chromate precipitates and adsorption of Cr(VI) onto the freshly formed copper-carbonate precipitates, both being highly pH dependent, were the main mechanisms responsible for Cr(VI) co-removal (Sun et al., 2003). The maximum co-removal of Cr(VI) with Cu(II) and close to 100% Cu(II) removal was observed at a pH of around 6.5 instead of 9.2 under drip-feed Na₂CO₃ dosing (Sun et al., 2003). Based on the results of the batch tests, a series of continuous-flow nucleated precipitation studies using fluidised sand strippers was further conducted under different pH and dosing techniques to confirm the optimum operating conditions for both Cr(VI) and Cu(II) removal in the continuous-flow system.

It is not the intention of this study to advocate the use of Cu(II) or other heavy metals as an agent to remove Cr(VI). However, since they coexist in most industrial wastewaters, it is advisable to use the available Cu(II) to maximise the co-removal of Cr(VI) first. The advantage of the technology is that the continuous single-step compact system using fluidised metal strippers allows the precipitates produced to coat on the media surface, in which precipitation of heavy metals, co-removal of Cr(VI), and solid-liquid separation occur. Precipitate dewatering is not required, and metals can be recovered by dissolving the metal-coated sands with acids. Therefore, the technology is simple in operation, space-

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