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Simultaneous removal of chromium(VI) and fluoride by electrocoagulation–electroflotation: Application of a hybrid Fe-Al anode

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HIGHLIGHTS

- A combined EC–EF process is used for simultaneous removal of Cr(VI) and fluoride.
- The EC step involves integrated reduction of Cr(VI) and coagulation of fluoride.
- In EF step, the separation solid/liquid was improved.
- The interest of hybrid anode is to avoid supplementary EC step.

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ABSTRACT

A combined two-step EC–EF process was designed to simultaneously remove Cr(VI) and fluoride from pretreated acidic semiconductor effluents. The EC step comprises integrated reduction of chromium(VI) with coagulation of fluoride, while in the EF step, clarification takes place. In EC step a hybrid Fe–Al was used as sacrificial anode and stainless steel as cathode. Initially, the effect of anodic material on EC–EF efficiency was investigated and it was found that the combination 2Fe–2Al gives the optimum results. Most of Cr(VI) removal was ascribed to iron plates, while fluoride removal was mainly ascribed to aluminum plates. Presence of coagulants enabled the removal of suspended solids which are present in initial solution. Effects of initial pH, current intensity, anions nature, chloride concentration and initial concentration on EC–EF process efficiency using hybrid anode were studied. The behavior of the hybrid anode depends on both iron and aluminum individual properties toward pollutants. Under optimum conditions, residual concentrations of Cr(VI) and fluoride and turbidity after EC–EF were found under national discharge standards.

1. Introduction

In semiconductor industry, a wide variety of chemicals are involved in wafers manufacturing [1,2]. Consequently, wastewater from semiconductor manufacturing units may contain numerous pollutants including suspended solids, heavy metals, fluoride, chelating agents, toxic solvents, dyes and salts [2]. Depending on the waste nature, many treatment techniques have been proposed. This includes biological [3], membrane [4] and photocatalytic methods [5,6]. The acidic wastes are of a particular concern [1]. Waste sulfuric, hydrofluoric, hydrochloric, phosphoric, nitric, and chromic acids are produced as a result of wafer surface etching. Particularly, in Secco and Yang etching processes [7,8] where formulations with HF/chromic acid are used. Thus, toxic ions like fluoride and Cr(VI) are found in concentrations much higher than permissible values in semiconductor effluents [9]. Fluoride limit discharge is 15 mg/L [10]. Depending on solution pH, Cr(VI) exists as highly soluble H_2CrO_4, $HCrO_4^-$, $Cr_2O_7^{2-}$ and CrO_4^{2-} species. Due to their high toxicity and mobility they can cause health and environment concern. Hence, concentration of Cr(VI) in industrial effluents is strictly controlled before being discarded [11]. A discharge limit value of 0.05 mg/L is set for Cr(VI) [12].

Almost all semiconductor industrial plants use adding calcium salt especially lime as pretreatment for such acidic wastes [9,10]. However, precipitation is insufficient to comply with environmental standards. Fluoride can only be reduced to 25–60 mg/L [13]. Poor settling of the resulting CaF_2 precipitates is a major difficulty which results in turbidity higher than permissible limits [1]. Moreover, effluents still do not meet the discharge standards for some pollutants such as chromium(VI). Thus, subsequent

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