Coagulation–flocculation mechanisms in wastewater treatment plants through zeta potential measurements

E.A. López-Maldonado [a,*], M.T. Oropeza-Guzman [a,b], J.L. Jurado-Baizaval [a], A. Ochoa-Terán [b]

[a] Centro de Investigación y Desarrollo Tecnológico en Electroquímica, Unidad Tijuana, Carretera libre Tijuana-Tecate km 26.5, esq. Blvd Nogales Parque Ind. El Florido CP 22444, Tijuana, B.C., Mexico
[b] Centro de Graduados e Investigación en Química del Instituto Tecnológico de Tijuana, Blvd. Alberto Limón Padilla s/n, Mesa de Otay, C.P. 22500, Tijuana, B.C., Mexico

HIGHLIGHTS

- A well planned polyelectrolyte dosing strategy plays a crucial role in successful coagulation–flocculation process.
- pZ–pH plots are a powerful tool to plan polyelectrolytes dosage and to discover coagulation–flocculation mechanisms.
- Previously prepared polyelectrolytes dispersions improved resulting water quality after a coagulation–flocculation process.

GRAPHICAL ABSTRACT
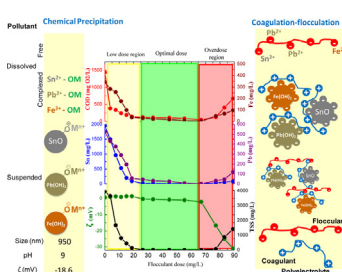
ARTICLE INFO

ABSTRACT

Based on the polyelectrolyte-contaminant physical and chemical interactions at the molecular level, this article analyzed and discussed the coagulation–flocculation and chemical precipitation processes in order to improve their efficiency. Bench experiments indicate that water pH, polyelectrolyte (PE) dosing strategy and cationic polyelectrolyte addition are key parameters for the stability of metal–PE complexes. The coagulation–flocculation mechanism is proposed based on zeta potential (ζ) measurement as the criteria to define the electrostatic interaction between pollutants and coagulant–flocculant agents. Polyelectrolyte and wastewater dispersions are exposed to an electrophoretic effect to determine ζ. Finally, zeta potential values are compared at pH 9, suggesting the optimum coagulant dose at 162 mg/L polydadmac and 67 mg/L of flocculant, since a complete removal of TSS and turbidity is achieved. Based on the concentration of heavy metals (0.931 mg/L Sn, 0.7 mg/L Fe and 0.63 mg/L Pb), treated water met the Mexican maximum permissible limits. In addition, the treated water has 45 mg O_2/L chemical oxygen demand (COD) and 45 mg C/L total organic carbon (TOC). The coagulation–flocculation mechanism is proposed taking into account both: zeta potential (ζ)–pH measurement and chemical affinity, as the criteria to define the electrostatic and chemical interaction between pollutants and polyelectrolytes.

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1. Introduction

The electroplating wastewater, in the semiconductor industry, contains dissolved and suspended heavy metals (such as Sn, Cr, Ni, Pb, and Cu, among others), making necessary to find a suitable

* Corresponding author. Tel.: +52 6646453278.
E-mail addresses: elopez@cideteq.mx, eduardo_a_lm@hotmail.com (E.A. López-Maldonado).

water treatment to remove them before disposal. Hazardous situation are challenged when dissolved and suspended heavy metals are not completely removed before being discharged into the sewage.

In recent years, several technologies have been developed to regulate the hazard of wastewater containing heavy metals and focusing in the decrease of wastewater volume and the improvement in recovered water quality [1,2]. Within the conventional physicochemical methods to treat electroplating wastewater, it can be mentioned: chemical precipitation [3–6]; coagulation–flocculation [3,7]; flotation [8,9]; electrocoagulation [10,11]; zeolites, clays and resins ion exchange [12–16] and membrane filtration (ultrafiltration, nanofiltration and reverse osmosis) [17,18]. In all these cases, wastewater content such as metals, organic matter (OM) and total suspended solids content are included.

Chemical precipitation has been applied to remove dissolved heavy metals. This method is based on the chemical reaction between the metallic cations and calcium hydroxide as precipitating agent resulting in the formation of insoluble compounds, and the subsequent solid separation by sedimentation or filtration [19].

The general reaction for this process is:

$$M^{n+} + nOH^- \rightarrow M(OH)_n \downarrow \qquad (1)$$

where M^{n+} and OH^- represents the dissolved metal ions and the precipitating agent, respectively, and $M(OH)_n$ is the insoluble metal hydroxide. Chemical precipitation is, in many cases, unable to comply the permissible limits due to the fact that metallic hydroxides in wastewater do not precipitate at the same pH [19], and depends on metal concentration.

The colloidal nature of wastewater and surface charge of the metallic hydroxide could make more difficult the solid–liquid separation, as well as the presence of organic complexing agents that reduce the removal effectiveness [6]. Even if the pH condition and solubility product are known, it is uncertain to calculate the solubility of heavy metals in electroplating wastewater [20–22]. It is well known that large amount of impurities, such as organic matter, make the metal solubility greater than that expected, mainly due to the chemical interactions between the metallic cations and organic matter [23].

Zeta potential (ζ) is an interfacial parameter related to the low solubility condition of dissolved metals when the isoelectric point is reached. There are inclusive precipitating agents that assist the formation of metal hydroxides by the zeta potential reduction of residual water [24]. In all cases, the formation of metal hydroxides depends on the change of surface charge as a function of pH [25–28].

Other chemical precipitation treatments have been tested in the last century, particularly those using sulfide (Na_2S); however, high cost and struggle in the disposal of toxic sludges discourage its use [29]. Also, sodium phosphate was used to precipitate a metal phosphate, but the concentration of residual phosphorus in the treated water exceeds the maximum allowable limit [19,30,31].

New technologies are oriented to mixed pollutants removal (i.e. particles, organic matter and metals simultaneously). In particular, the combined coagulation–flocculation process is addressed to eliminate suspended particles and insoluble substances. Even though, removal of toxic heavy metals from electroplating wastewater by coagulation–flocculation remains being a challenge due to the mixed of chemicals such as organic matter, suspended particles and metallic cations. Until now, there are no physicochemical method to find the optimal dose for each contaminant removal by coagulation–flocculation, unless Jar test. However, exploring the chelating ability of coagulant and flocculant polyelectrolytes (PEs) is an alternative to optimize the removal lof various the types of pollutants [32].

This paper explores the chelating ability of commercial coagulant and flocculant polyelectrolytes (PEs) used in real wastewater treatments. Selected conditions for coagulation–flocculation are presented, as well as removal mechanisms suggested for suspended solids, organic matter and metallic cations for four different strategies of PE dosing.

To explain the mechanisms and interfacial phenomena occurring during coagulation–flocculation process under various physicochemical conditions, four different sets of experiments were planned and developed. The mechanism elucidation of PE–pollutants interactions can be used to set up the optimal process conditions for wastewater treatment.

The first of four sets of experiments was the characterization of electroplating raw wastewater to compare against the permissible limits of applicable Mexican environmental regulation (NOM-002-SEMARNAT-1996); the second was to construct the $\zeta = f(pH)$ graphs to establish different PE dosing strategies; and third, identify the coagulation–flocculation regions for the removal of metals, suspended solids and organic matter.

The experimental strategy, to study the conditions of coagulation–flocculation process was to examine the profiles of $\zeta = f(pH)$ of commercial PEs used in semiconductor assembly waste water treatment plants. Once the isoelectric point of the coagulant and flocculant was determined, as well as that of the sampled wastewater, PE dosing was studied at different pH values. In parallel the effect of using an interpolyelectrolyte complex flocculation in the selected window was tested. Finally, the effect efficiency of coagulant dose in the flocculation selected window by the dual flocculation process was established. Based on the nature of the interfacial phenomena that occur between pollutants and PEs in the coagulation-flocculation process and the electrochemical nature of the measurements of zeta potential, the experimental methodology used allowed us to determine the mechanisms of coagulation–flocculation.

2. Materials and methods

2.1. Reagents

Semiconductor industry commercial polyelectrolytes Polydadmac (OPTIFLOC C-1008) and Flocculant (Trident 27,506) were used [32]. Commercial testing water quality reagents for Hach® methods were used. All other reagents used in this work were reagent grade.

2.2. Methods

2.2.1. Wastewater sampling in the assembling semiconductor industry

The wastewater sampling protocol in the assembling semiconductor industry was followed as recommended by Mexican sampling standard (NMX-AA-003-1980). A detailed chemical composition is uncertain due to the large amount of chemical mixtures employed in the electroplating baths [33]. Sampling planning was made in accordance to regulation parameters, selected electroplating process knowledge and water treatment control parameters. Included parameters are: metals (Sn, Pb and Fe), total suspended solids (TSS), turbidity, electrical conductivity (EC), zeta potential (ζ), particle size, color, pH, chemical oxygen demand (COD), total organic carbon (TOC), biochemical oxygen demand (BOD_5) and total nitrogen (TN).

2.2.2. Preparation of wastewater dispersions

The wastewater dispersions were prepared by diluting 5 mL of raw wastewater with deionized water in a 50 mL volumetric flask. Since the electroplating process was in continuous