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A novel combined electrochemical system for hardness removal

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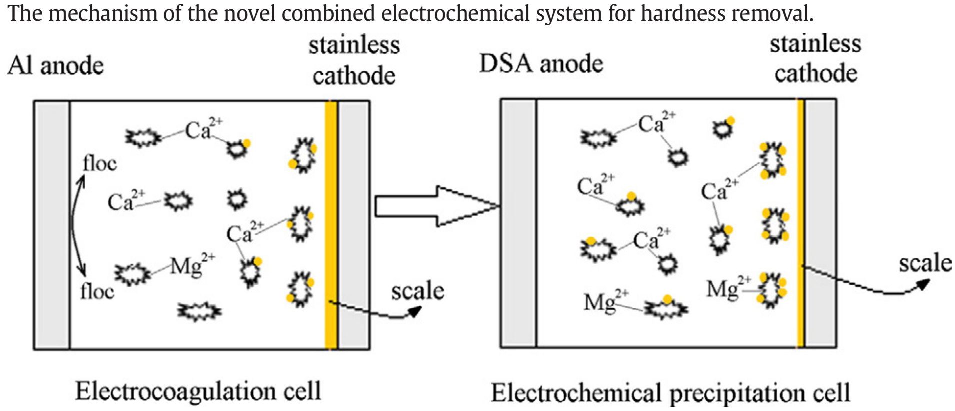
HIGHLIGHTS

- A novel concept of electrochemical system was established for hardness removal.
- The total hardness removal was increased for the large improvement of floc removal.
- The new system had lower operating cost than electrochemical precipitation process.
- The new system produced less sludge than electrocoagulation process.

GRAPHICAL ABSTRACT

The mechanism of the novel combined electrochemical system for hardness removal.



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ABSTRACT

A novel electrochemical system was proposed to remove hardness species, by combining the conventional electrocoagulation process and electrochemical precipitation process. The results showed that the new system had excellent synergistic effects. The little amount of Al floc produced in electrocoagulation cell enhanced the hardness removed by floc in electrochemical precipitation cell by 224.65% which increased the total hardness removal in the electrochemical precipitation cell by 69.16%. Meanwhile, the amount of deposit on the cathode surface in electrochemical precipitation cell was decreased by 22.79%, which would delay the cathode inactivation in practical application. The operating cost of the new combined electrochemical system was reduced by 53.09% than that of the conventional electrochemical precipitation process. And the production of sludge was nearly three times decreased in the new system than that in the conventional electrocoagulation process, for the lower current density. Therefore, this new proposed system is a beneficial technology for hardness reduction, which can overcome the drawbacks of the two conventional processes.

1. Introduction

Scaling is a big technical challenge and big financial burden for different industrial operators. It can reduce boiler power output by 10–20% and thermal efficiency by 10% [1–4], plug the pipeline [5,6], and even make more shut-downs [7]. The usual scale control methods applied in water desalination include: adding anti-scalant, which always contaminates the water source during preventing scaling [8]; ion exchange, which generates large volumes of concentrated solutions of acids or salts and the resin regeneration is a practical problem [9–13]; chemical precipitation (usually lime softening), which produces a high-volume lime sludge stream [14,15]. In many cases, the scale is predominantly due to the alkaline precipitation. One of the techniques which have been studied widely is electrochemical precipitation.

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1.1. Electrochemical precipitation

The basic principle of electrochemical precipitation process is to remove hardness species by creating a high pH environment around the cathode by water and oxygen reduction reactions which release hydroxyl ions.

The cathodic reactions are:

$$2H_2O + 2e^- \rightarrow H_2\uparrow + 2OH^-$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-.$$

The scale precipitation reactions are:

$$Ca^{2+} + HCO_3^- + OH^- \rightarrow CaCO_3\downarrow + H_2O$$

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2\downarrow.$$

The main anodic reactions are:

$$2H_2O \rightarrow 4H^+ + O_2 + 2e^-.$$

Although electrochemical precipitation method has been reported widely [16–18], industrial application of this technique is rather limited. The limitations are the high cathode area requirement which is the dominant part of high cost, and the burdensome cleaning of cathode surface [19–22].

1.2. Electrocoagulation process

The traditional principle of electrocoagulation process regards the pollutant removal as a complex process including physical and chemical reactions. The following reactions describe electrocoagulation process in relation to aluminum electrode:

The anodic reactions are:

$$A1 \rightarrow A1^{3+} + 3e^-$$

$$A1^{3+} + 3OH^- \rightarrow A1(OH)_3.$$

The cathodic reactions are:

$$2H_2O + 2e^- \rightarrow H_2\uparrow + 2OH^-.$$

The scale precipitation reactions are:

$$Ca^{2+} + HCO_3^- + OH^- \rightarrow CaCO_3\downarrow + H_2O$$

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2\downarrow.$$

In addition to precipitation of hardness species on the cathode surface, the adsorption of Ca^{2+} and Mg^{2+} to the $Al(OH)_{3n}$ floc produced from anode surface also exists [23]. The electrocoagulation process for removal of hardness was studied rather less than electrochemical precipitation [24,25]. The single process of electrocoagulation under low current density can't reach the goal removal rate according to our experiment (data not shown). Although higher current densities contribute to higher removal rates, higher sludge production would come up which is not environmentally friendly.

1.3. The novel combined electrochemical system

On understanding the mechanism of the two conventional electrochemical methods, a novel combined electrochemical system was proposed, shown in Fig. 1. In the new system, the water was firstly treated by electrocoagulation cell, and then immediately flowed into electrochemical precipitation cell. The following is the mechanism of this novel system in detail.

In electrocoagulation cell, Al^{3+} produces from the Al anode surface and aggregates to form a variety of polymeric structures (floc). The floc which is surface charged provides electrostatic attraction for Ca^{2+} and Mg^{2+}, which involve mainly physical adsorption [23]. Then, the floc carrying Ca^{2+} and Mg^{2+} migrates to the boundary layer near the cathode surface where the floc can provide extensive surface for hardness precipitation, rather than the restricted area of the cathode. In this cell, very low current density was needed avoiding a large amount of sludge production (the limitation of electrocoagulation process).

In electrochemical precipitation cell, the adsorption of Ca^{2+} and Mg^{2+} on the floc surface might be enhanced, for the floc surface modification by electric field in the cell. In addition, more $CaCO_3$ and $Mg(OH)_2$ would precipitate on the floc surface or be swept by the colloid net, resulting in advisable reduction of the scale on the cathode surface. In other words, the removal of hardness in electrochemical precipitation cell would partly transfer to the liquid phase removal from the cathode surface deposition which could delay the cathode inactivation.

The main objective of the present paper was to describe a novel combined electrochemical system and confirm the proposed function mechanism. The effects and economic cost will be compared between the novel combined electrochemical system and the two single processes (electrochemical precipitation process and electrocoagulation process).

2. Materials and methods

Three types of processes were conducted, as shown in Fig. 2, to compare the effects and economic cost of different systems. All feed solutions through the electrochemical cells were in the once-through mode which is usually adopted in practical application.

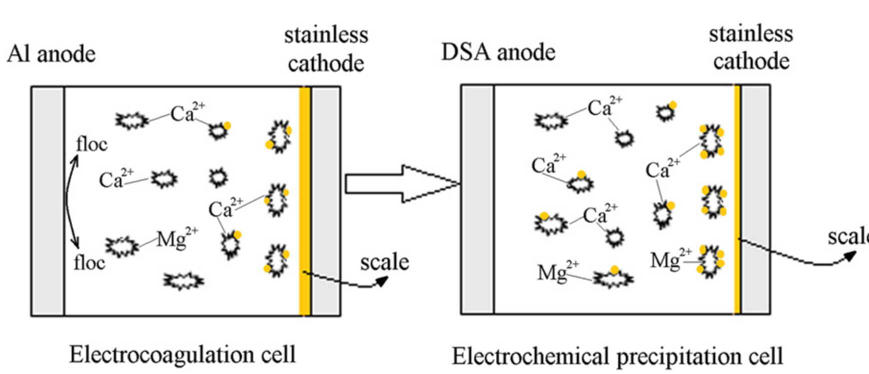

Fig. 1. The mechanism of the novel combined system.