Desalination 381 (2016) 8–14

Contents lists available at ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal

Hardness removal by a novel electrochemical method

Su-li Zhi, Ke-qiang Zhang *

Agro-environmental Protection Institute, Ministry of Agriculture, Tianjin 300191, China

HIGHLIGHTS

- A novel concept of electrochemical method was proposed for hardness removal.
- The synergistic removal rate and the sum removal rate were compared.
- The optimal operating condition was determined by studying influence factors.
- The relationship of different economic parts was established for the novel method.

ARTICLE INFO

Article history:
Received 22 July 2015
Received in revised form 26 October 2015
Accepted 6 December 2015
Available online 17 December 2015

Keywords:
Hardness
Electrochemical treatment
Synergetic effect
Difference value

ABSTRACT

A novel electrochemical system was proposed to remove hardness species, which has synergistic effect of the conventional electrocoagulation (EC) and electrochemical precipitation (EP). The synergistic removal rate and the sum removal rate of two conventional methods were compared, and the difference value of the two removal rates was used to determine the optimum operating conditions. The results showed that the optimum synergistic effect was obtained when the current density of EC cell was 20 A/m^2, the current density of EP cell was 250 A/m^2, the consistent flow rate was 120 ml/min, the pH value was 7.2, the water temperature was 60 °C, the recycle time was 130 min, and the initial hardness concentration lower was better. The order must be EC and then EP to have the synergistic effect after comparing the removal rates of different processes. The total cost of the novel system was divided into three parts: Al cost of 11.02%, power cost of 85.33% and DSA cost of 3.65% under the optimum conditions. Then the variations of power cost, Al cost and Dimensionally Stable Anodes (DSA) cost with current density, were analyzed to provide a reference for industrial operators.

1. Introduction

Water hardness generally originates from the existence of various cations such as Ca^{2+}, Mg^{2+} and so on. They are not only detrimental to human health (causing nephritis), but also extremely troublesome for industrial production processes. It was reported that more than 85% of boilers in the United States have hard water supplies [1]. The hardness ions can be concentrated beyond the solubility limit resulting in scale deposition, for the evaporation of water [2]. Scaling on the surface of heat exchanger reduces boiler power output by 10–20%, decreases thermal efficiency by 10% [3–6], plugs the pipeline [7], and even makes more shut-downs [2].

Traditional methods to reduce hardness ions are mainly chemical treatments [8–14] which usually introduces other ions into water source causing water pollution. In comparison, electrochemical treatment has many advantages: introducing no contaminants in the water source; producing no large volumes of concentrated effluents and solid waste; easily being operated in practical application. Therefore, it arouses more and more interest for researchers in the field of hardness removal. There are usually two kinds of electrochemical treatments to remove water hardness. One is electrochemical precipitation (EP), which removes hardness ions through creating a high pH environment around the surface of cathode by the following reactions:

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

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

The alkaline environment leads to the precipitation reactions as follows:

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

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

The main anodic reactions are electrolytic reaction of H_2O, generating oxygen on Dimensionally Stable Anodes (DSA).

The other one is electrocoagulation (EC) which removes hardness ions not only by scale precipitation on cathode surface just as in EP,

* Corresponding author.
E-mail address: zhisuli83@163.com (S. Zhi).

http://dx.doi.org/10.1016/j.desal.2015.12.002
0011-9164/

but also by the adsorption of Ca^{2+} and Mg^{2+} to the $Al(OH)_{3n}$ floc produced from Al anode surface as follows [15]:

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

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

However, each of the two electrochemical scaling control methods has its own disadvantages: EP needs high cathode area to sufficiently precipitate hardness ions, which inevitably results in high cost and burdensome cleaning of cathode surface [16,17]; EC always produces large volume of sludge for Al anode dissolution under high current density, which is not environmentally friendly.

In order to overcome the limitations of each electrochemical method, a novel electrochemical method was proposed in our previous study [18]. Simply, the novel electrochemical system was established by combined EC and EP; under a very low current density, EC produced a little amount of sludge; but the sludge could provide extensive surface for hardness precipitation, which avoided precipitation on the cathode surface; finally, the synergy of EC and EP resulted in high precipitating rate and low cost. This paper furthered the study by comprehensively analyzing the effects of different influencing factors for the novel method. The synergistic removal rate, sum removal rate and the difference value of the two removal rates were investigated to determine the optimum conditions of the novel system. In addition, the relationship of economic parts was analyzed to guide the industrial investment.

2. Materials and methods

Fig. 1 shows the four processes to be studied in the experiment. The EP × EC process represents the synergetic effects of EP and EC. It was conducted by pumping the water into EP first and then into EC immediately. The EC × EP process represents the synergetic effects of EC and EP. Similarly, the water was pumped into EC first and then into EP immediately. These two processes aimed at determining the order of the EC and EP. The EC + EP or EP + EC process represents the sum effects of EC and EP. Differently, the water was pumped into EC (or EP) and settled for 60 min before into EP (or EC), which avoided the aluminum floc generated in EC pumping into EP. In the most experimental runs except for the recycle time, the feed water was in the once-through mode which is usually adopted in practical application. Each experiment lasted at least 5 residence times to ensure a steady state condition of the cells, and then the samples were taken. The data was the average of at least three samples.

The condition of electrochemical cells, feed water and samples was same as our previous report [18]. The removal rate in the study might be limited by electrode area and experiment conditions, but the purpose of the study focused on the synergetic effect which was evidenced by the different removal rates of different processes. The system structure would be investigated in our further study, to establish an appropriate scale system under the novel concept.

3. Results and discussion

The synergetic effects of EC and EP were verified through comparing the removal rates between EC × EP (the synergetic removal rate) and EC + EP (the sum removal rate). And the optimum synergetic effects were determined according to the difference value of the removal rates between EC × EP and EC + EP.

3.1. Effect of influence factors

3.1.1. Effect of current density

Fig. 2 shows the variation of removal rates with current density in EC cell (J_1) under different processes. It can be seen that the removal rates of EC × EP were higher than those of EC + EP under the same current densities, which implied that the synergetic effects of EC and EP could be realized by combining the EC and EP. Obviously, the removal rates increased with the increase of current density of EC cell. According to the mechanism of the proposed electrochemical method, the increase of current density of EC cell directly resulted in more OH^- producing on the cathode surface, which inevitably led to more hardness species precipitating on the surface of cathode. Moreover, higher current density of EC cell generated more aluminum floc in the solution which could adsorbed more hardness species. However, from the variation of difference value of removal rates, we can see that 20 A/m^2 ensured a highest difference value, which proved the best synergetic effects occurred at current density of 20 A/m^2.

Fig. 3 shows the removal rates and difference value under different current densities of EP cell (J_2). Similarly, higher current density resulted

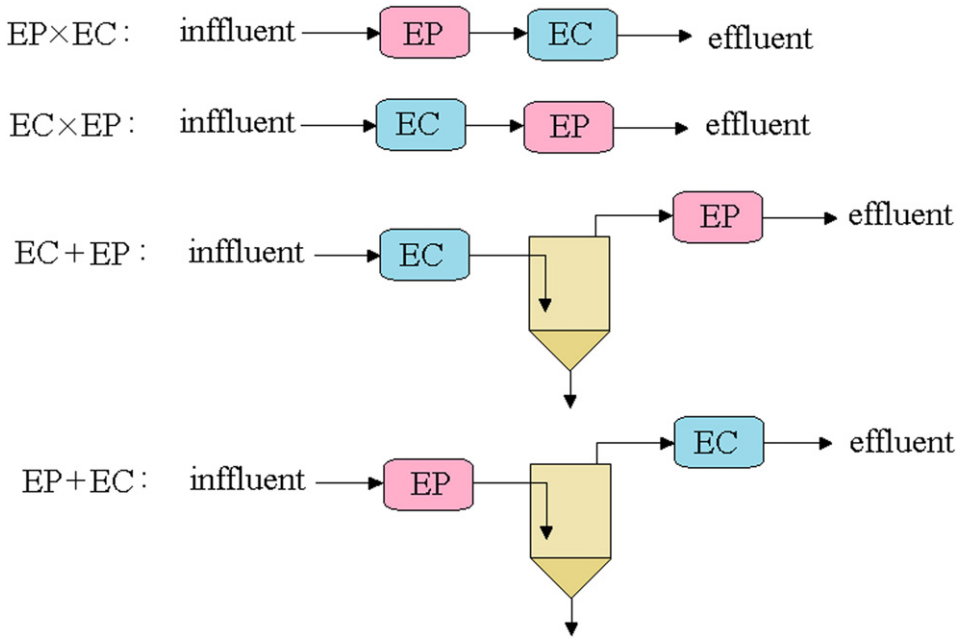

Fig. 1. The flow diagrams of different processes.