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THE EFFICIENCY OF ELECTROCOAGULATION PROCESS USING ALUMINUM ELECTRODES IN REMOVAL OF HARDNESS FROM WATER

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ABSTRACT
There are various techniques for removal of water hardness each with its own special advantages and disadvantages. Electrochemical or electrocoagulation method due to its simplicity has gained a great attention and is used for removal of various ions and organic matters. The aim of the present study was to investigate the efficiency of this technique in removal of water hardness under different conditions. This experimental study was performed using a pilot plant. The applied pilot was comprised of a reservoir containing aluminum sheet electrodes. The electrodes were connected as monopolar and a power supply was used for supplying direct electrical current. Drinking water of Kerman (southeast of Iran) was used in the experiments. The efficiency of the system in three different pH, voltages and time intervals were determined. Results showed the efficiency of 95.6% for electrocoagulation technique in hardness removal. pH and electrical potential had direct effect on hardness removal in a way that the highest efficiency rate was obtained in pH=10.1, potential difference of 20 volt and detention time of 60 minutes. Considering the obtained efficiency in the present study, electrocoagulation technique may be suggested as an effective alternative technique in hardness removal.

Keywords: Electrocoagulation technique, Hardness removal, Aluminum electrode, Electrochemical technique

INTRODUCTION
Water hardness creates a lot of problems for life and industry. Except calcium and magnesium, iron, manganese and strontium and some other metals can cause water hardness too, but their amount in comparison to the amount of calcium and magnesium can be ignored (Schaep *et al*., 1998; HDR Engineering Inc, 2001; Yildiz *et al*., 2003; Park *et al*,. 2007). Considering problems of water hardness, its removal is essential (Kawamura, 2000).

There are various techniques for the removal of water hardness, such as using chemical substances and ion exchange resins (Schaep *et al*., 1998; Kabay *et al*., 2002; Yildiz *et al*., 2003; Gasco and Me´ndez, 2005; Park *et al*,. 2007). Applying each of these techniques has undesirable effects on the quality of product water. In the process of ion exchange, sodium concentration of water increases that is harmful for patients with hypertension or cardiovascular diseases who have to consume sodium limit diet. Ion exchange processes cannot be applied for removal of water hardness in large water treatment plants (Abbes *et al*., 2008). Using lime for softening causes an increase in permanent water hardness. On the other hand, great amount of produced sludge causes clogging of filters and water distribution systems.

Using these appliances requires skill and addition of specified amount of lime and sodium carbonate to the system (Degremond, 2002; Bazrafshan *et al*., 2007). In the process of liming, coagulants such as alum or ferric chloride are used to increase the weight of insoluble particles and consequently sedimentation velocity (Degremond, 2002). This technique in addition to its economic cost, has

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undesirable health effects such as increasing the risk of Alzheimer disease, moreover, lime increases water pH. In order to improve the efficiency of chlorine in the process of disinfection, water pH after hardness removal should be decreased to <7.8 and this requires increase in acid consumption (Kawamura, 2000; Park *et al*., 2007). Coagulants in addition to increasing the amount of sludge production, increase the total solids in the effluents (Ramesh *et al*., 2007). Adsorption process is also used for hardness removal. This process due to adsorbent loss during the process and the necessity of backwashing has also gained less attention (Gasco and Me´ndez, 2005; Ramesh *et al*., 2007). Use of membranes, has the problem of scaling and frequent membrane fouling (Schaep *et al*., 1998; Park *et al*., 2007; Walha *et al*., 2008).

Electrochemical or electrocoagulation process due to its simplicity has gained great attention and is used in removal of various ions and organic matters (Bazrafshan *et al*.,2007). This process includes a cell with metal anode (mostly iron and aluminum) and uses direct electrical current (Xiong *et al*., 2001; Daida, 2005; Kim *et al*., 2007). This process has three stages (Ramesh *et al*.,2007; Ghernaout *et al*., 2008)

1. Coagulants forming due to anode electrical oxidation
2. Destabilizing pollutants and suspended substances and emulsion breaking
3. Combining instable particles to form floc (Ramesh et al., 2007; Ghernaout et.al., 2008)

Destabilization mechanisms in this process include electrical double-layer compression, adsorption and charge neutralization, enmeshment in a precipitate and inter-particle bridging (Druiche *et al*., 2008; Kim *et al*., 2007).

If in this process M is considered as anode, the following reactions will occur:

In anode:

$$M_{(s)} \rightarrow M_{(aq)}^{n+} + ne^- \quad (1)$$

$$2H_2O+2e^- \rightarrow 4H^+_{(g)} + O_{2\,(g)} + 4e^- \quad (2)$$

In cathode:

$$M_{(aq)}^{n+} + ne^- \rightarrow M_{(s)} \quad (3)$$

$$2H_2O+2e^- \rightarrow H_{2\,(g)} + 2OH^- \quad (4)$$

If iron and aluminum electrodes are used, Fe^{+3} and aluminum are produced.These metal ions after reaction with hydroxyl ions will produce metal hydroxides or poly-hydroxides (Ramesh *et al*., 2007). For instance, aluminum in water produces Al $(H_2O)_6^{3+}$, Al $(H_2O)_5OH^{2+}$, Al $(H_2O)_4OH^{1+}$ or monomer or polymer strains of :Al $(OH)^{2+}$, $Al_2\ (OH)_2^{4+}$, $Al_6\ (OH)_{15}^{3+}$, $Al_{13}\ (OH)_{34}^{5+}$. These compounds increase the elimination efficiency (Jiang *et al*., 2002; Bazrafshan and Mahvi, 2007; Kim *et al*., 2007; Druiche *et al*., 2008). The final compound of the eliminated matter by this process depends on parameters such as electrode type of matter, electrode shape (Mavrov *et al*, 2006; Druiche *et al*, 2008).

In recent decades, three dimensional electrodes have been used (instead of two dimensional) that are suitable for the treatment of low concentration pollutants (Daida, 2005; Ghernaout *et al*., 2008). In this process because of hydrogen release from cathode and oxygen release from anode, flotation takes place (Jiang *et al*., 2002; Mavrov *et al*., 2006). Moreover, the adsorption rate of produced hydroxides by this process is 100 times as much as hydroxides produced through chemical processes and they do not produce secondary pollutants (Gurses *et al*., 2002).

In addition to the above reactions, the following reactions may also occur in cathode in high acidity conditions:

$$HCO_3+OH^- \rightarrow CO_3^{2-}+H_2O \quad (5)$$

$$CO_3^{2-}+Ca^{2+} \rightarrow CaCO_3 \quad (6)$$

$$CO_3^{2-}+Mg^{2+} \rightarrow MgCO_3 \quad (7)$$

calcium carbonate and magnesium carbonate are settled on cathode (Mameri *et al*., 1998). Usually underground water contain high concentration of hardness, nitrate and fluoride either naturally or by agricultural activities (Mahvi *et al*., 2005; Nouri *et al*., 2006,) and it seems that electrocoagulation process is suitable for removal of these matters (Bazrafshan *et al*., 2006)

The aim of this study was to investigate the capability of electrocoagulation process in removal of water hardness as an alternative technique and to determine the optimum pH and electrical potential.

MATERIALS AND METHODS

The study was conducted by using a pilot plant with 6 aluminum electrodes, 15mm apart from eachother (the range of distance used in industry is 0.5-3cm) (Kim *et al*., 2002; Hu *et al.,* 2005). Pilot equipments included a power source (alternative to direct current converter), six commercial aluminum electrodes with dimensions of 10×10 cm and a glass reservoir with the efficient volume of 1.3L.

Electrodes were connected as monopolar. Hardness rate was determined by EDTA titrimetric method (APHA /AWWA /WEF, 1999). In order to achieve the desired pH, sulfuric acid (1N) or NaOH (1N) were used (Kim *et al*., 2002). pH rate was determined by Hanna digital instrument. Water samples were prepared from drinking water of Kerman located in southeast of Iran.

The total hardness and calcium hardness of the water were respectively 464 and 316 mg/L, as calcium carbonate. The prepared solutions with adjusted pH were injected into the reactor and sampling from the reactor was done in different time intervals of 20 minutes. After passage from filter paper, pH, total hardness and calcium hardness were measured. In order to determine the effect of voltage on process efficiency in this study, the efficiency of hardness removal in different electrical potentials of 5, 10 and 20 volt and pH of 5.3, 7.2 and 10.1 and time intervals of 20, 40 and 60 minutes were determined.

RESULTS

Figs 1, 2, and 3 represent the percent of total hardness and calcium hardness removal in different pH, electrical potential and time intervals. As it is seen, removal efficiency in pH=5.3, electrical potential of 20 v and 60 minutes has been 47% (Fig. 1). In pH=7.2 the removal efficiency has increased and the maximum efficiency in this pH and in electrical potential of 20v and time interval of 60 minutes has been 80.6% (Fig. 2). In pH=10.1, the highest removal efficiency was 95.6% that has been achieved in potential difference of 20v and time interval of 60 minutes (fig. 3).

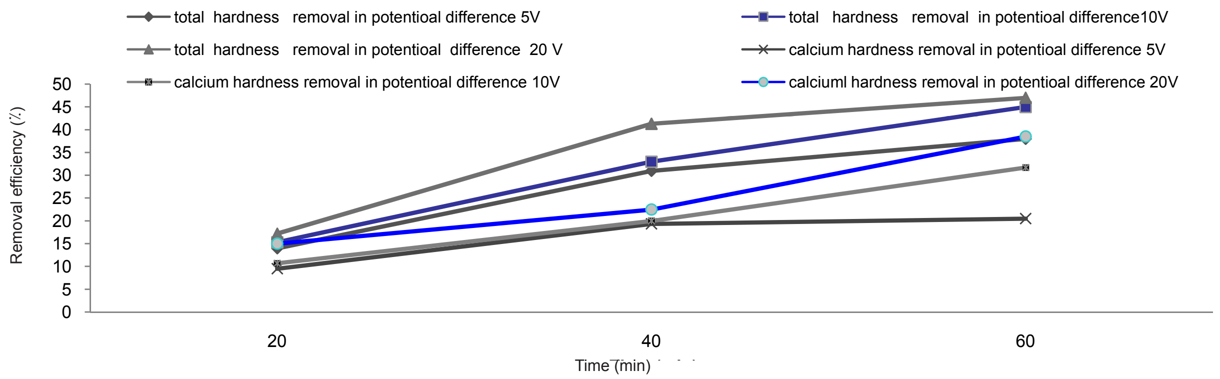

Fig. 1: Efficiency of total and calcium hardness removal in pH=5.3 and different voltages

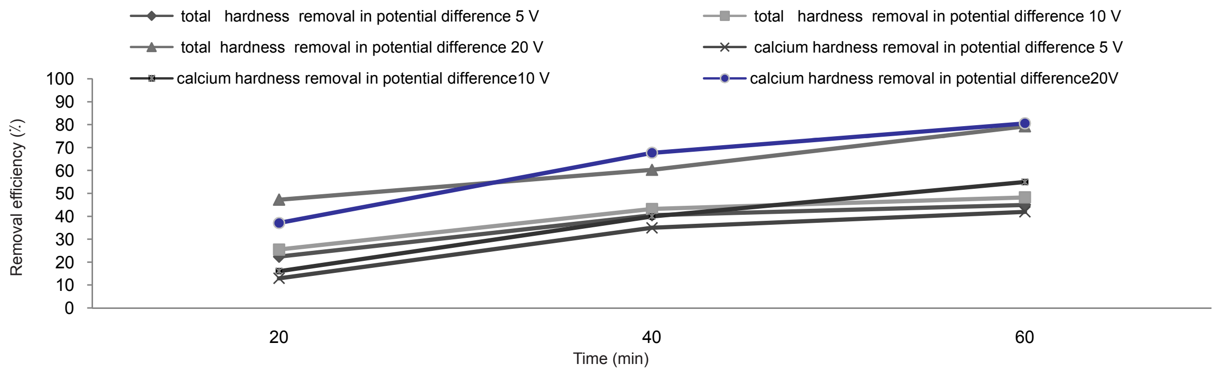

Fig. 2: Efficiency of total and calcium hardness removal in pH=7.2 and different voltages

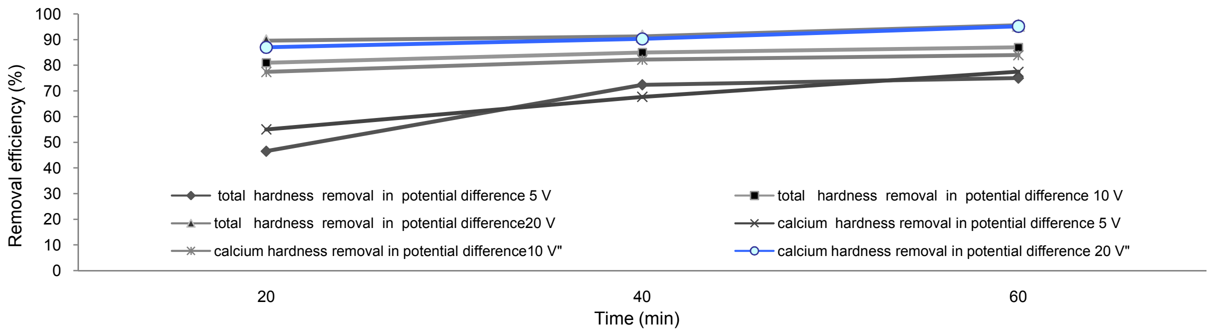

Fig. 3: Efficiency of total and calcium hardness removal in pH=10.1 and different voltages

DISCUSSION

Effects of pH

With pH increase, the rate of hardness removal increase since the effect of pH on coagulants depends on the produced reactions on different conditions.

In neutral conditions:

$$3Al_{(s)} + 8H_2O_{(1)} \rightarrow Al(OH)_{2(s)} + 2Al(OH)_3 + 4H_{2(g)} \quad (8)$$

In acid conditions:

$$2Al_{(s)} + 6H_2O_{(1)} \rightarrow O_2(g) + 4H_{2(g)} + Al(OH)_{2(s)} \quad (9)$$

In alkali conditions:

$$2Al_{(s)} + 6H_2O \rightarrow 2Al(OH)_{3(s)} + 3H_2O_{(1)} \quad (10)$$

Here, Al $(OH)_3$ and Al $(OH)_2$ settle while, H_2 moves upward and causes flotation. As reactions show, in acidity condition Al $(OH)_2$ and in alkali condition Al $(OH)_3$ are produced. Since Al $(OH)_3$ has higher weight and density, it settles faster and has higher efficiency. Therefore, it acts better in enmeshment in a precipitate (Hua *et al*., 2003; Daida, 2005; Ghernaout *et al*., 2008). This fact has also been confirmed by Ghernaout in his study in 2008 on Escherichia coli removal from surface water by electrocoagulation method (Ghernaout *et al*., 2008). Hence, based on the results of the present study and previous studies electrocoagulation process can act as a pH moderator (Kim *et al*., 2002; Bazrafshan. *et al.*, 2007).

The effect of electrical potential

With increase of electrical current, the efficiency of hardness removal increases. In high voltages, size and growth rate of produced flocs increase and this in turn affects the efficiency of the process (Kim *et al*., 2002; Zhu *et al*., 2005). By electrical potential increase the amount of oxidized aluminum increases and consequently hydroxide flocs with high adsorption rate increase and this leads to an increase in the efficiency of hardness removal (Ranta *et al* ., 2004; Bazrafshan *et al*., 2007). On the other hand, by electrical current increase, the density of bubbles increases while their size decreases.

Since the effective surface and retention time of larger bubbles are less comparing to small ones, so density increase and bubble size decrease the flotation efficiency increases (Hu *et al*., 2005). Of course, sometimes surfactants are used to decrease the surface tension of solutions and consequently the size of bubbles. With decrease of electrical current, the required time for achieving similar efficiencies increases. These findings are in line with the results of Ranta Kumar et al study in 2004 in relation to arsenic removal by electrocoagulation method and the results of Bazrafshan et al study in 2007 in relation to the capability of electrocoagulation method with Aluminum electrodes in Cr^{6+} removal (Ranta *et al* ., 2004; Bazrafshan *et al*., 2007). Generally, the electrical potential of 20v is required for achieving the desired efficiency. Of course, electrical conductivity of electrodes affects also the efficiency. The rate of electrical conductivity has a direct relation with the distance of electrodes. With increasing electrodes distance, electricity consumption increases that leads to the increase of removal efficiency (Daida, 2005; Kim *et al*., 2005).

The effect of retention time

Increase in retention time in the case of constant potential difference and pH, increases the efficiency of hardness removal and this is because of precipitation of flocs that cause removal of hardness particles. In addition, in this process the rate of mixing, affects efficiency since this mixing causes flocs growth and decreases retention time (Kim *et al*., 2005).

The results show that most of the hardness has been removed in the beginning of process and this has also been found by Kumar et al in their study about the efficiency of Arsenic removal, Chaudhary et al (2003) and Bazrafshan et al (2007) in their studies on Cr^{+6} removal by electrocoagulation process (*Chaudhary et al.,* 2003; Ranta *et al*., 2004; Bazrafshan *et al*., 2007).

The results of the present study and other related studies show that electrocoagulation process in comparison to other techniques has some important advantages such as simple equipments, convenient operation, lower retention time, decrease or no need for using chemical matters, rapid sedimentation of produced flocs and less sludge production (Kim *et al*., 2002 Hu *et al*.,2005; Kobya *et al*., 2006; Ramesh *et al*.,2007; Druiche *et al*., 2008;). On the other hand it seems that electrocoagulation process cannot be applied for removal of water hardness in large water treatment plants.

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