Boron Removal From Shat Al-Arab River Water Using Electrocoagulation

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ABSTRACT

  Shat Al-Arab is a river located at the south of Iraq. Boron concentration has increased significantly recently due to the drought season which makes water from the Arabian Gulf pour into Shat Al-Arab. Boron concentration, as high as 5 mg/l, was detected in this river. This is 10 times the allowable drinking water concentration for boron according to WHO and the Iraqi drinking water guidelines, i.e. 0.5 mg/l.

  Experiments were conducted to determine the ability of electrocoagulation technique to reduce boron concentrations in synthetic water of 5 mg Boron/l and conductivity of 2000 µS/cm to the required level in drinking water. Experimental setup was prepared to determine the effects of several operating parameters on the optimum operation for the electrocoagulation. In addition, the technique was compared with chemical coagulation, using Poly-Aluminum-Chloride, Aluminum Sulphate, and Ferric Chloride.

  The experiments revealed that chemical coagulation has a very low efficiency (about 12%) that renders it unsuitable as a pretreatment for existing (or for the future) desalination units. On the other hand, electrocoagulation experiments showed a maximum boron removal efficiency of 40% at a current density of 5 mA/cm^2, operating time of 30 minutes, and pH of 8.

Keywords: Electrocoagulation, Boron removal, coagulation, Shat Al-Arab

إزالة البورون من مياه شط العرب باستخدام التخثير الكهربائي

الخلاصة

شط العرب هو نهر يقع في جنوب العراق، وقد زاد في الآونة الأخيرة تركيز البورون في مياهه بشكل ملحوظ بسبب موسم الجفاف الذي جعل مياه خليج العربي تصب في شط العرب. تم الكشف عن البورون في مياه النهر ولوحظ وجود تركيز عالي يصل إلى 5 ملغم/لتر، ويبلغ هذا 10 أضعافالتركيز المسموح به في مياه الشرب وفقا لمنظمة الصحة العالمية والمواصفة القياسية لمياه الشرب في العراق والبالغة (0.5 ملغم/لتر).

تم إجراء تجارب لتحديد قدرة تقنية التخثير الكهربائي على خفض البورون في مياه صناعية تحتوي
على تركيز 5 ملغم/لتر بورون وتوصيلية مقدارها 2000 ميكرو سيمنز/سم إلى الحدود المسموح بها
في مياه الشرب. تم إعداد التجارب لتحديد الآثار المترتبة على عدد من المعايير على التشغيل الأمثل
للتخثير الكهربائي. بالإضافة إلى ذلك، تمت مقارنة هذه التقنية مع تقنية التخثير الكيميائي التقليدية،
وذلك باستخدام ثلاث أنواع من المخثرات؛ هي بولي كلوريد الالمنيوم، و كبريتات الألومنيوم، وكلوريد
الحديديك. كشفت التجارب أن للتخثير الكيمياوي كفاءة منخفضة للغاية (حوالي 12%) مما يجعل هذه
التقنية غير صالحة للاستعمال كمعالجة أولية لوحدات تحلية المياه القائمة (أو المستقبلية). من ناحية
أخرى، أظهرت تجارب التخثير الكهربائي لإزالة البورون كفاءة عضمى بمقدار 40% عند استخدام
تيار كهربائي بكثافة 2 ملي امبير/سم2، ووقت تشغيل 30 دقيقة و دالة حمضية (pH) مقدارها 8.

الكلمات المرشدة: التخثير الكهربائي، إزالة البورون، التخثير، شط العرب

INTRODUCTION

Boron is a naturally occurring element that is widely distributed at low concentrations in the environment. Unlike most of the elements in sea water, boron is not ionized (i.e. it has no charge). Boron takes two forms in water (depending on pH value), Boric acid and borate ion. Boric acid dissociation is a function of pH, above pH 9.24 the anion $B(OH)^-$ is predominant, while below pH 9 the uncharged species is predominant [1,2,3]. Boric acid and borate salt have extensive industrial use in the manufacture of glass and porcelain, in wire drawing, production of leather, carpet and photographic chemicals.

Although boron is essential for plant growth, in excess of 2.0 mg/l in irrigation water, it is harmful to certain plants. Other plants may be affected adversely by concentration as low as 1.0 mg/l [4]. Food and agriculture organization in United Nations (FAO) imposed a regulation on the concentration of boron in irrigation water to be between 0.7-3 mg/l [5]. The world health organization (WHO) recommends a maximum boron concentration as low as 0.5 mg/l for drinking water. Iraqi drinking water guideline adopted the same value [6].

Several technologies have been used to lower boron concentration in water and wastewater. One of the important technologies used successfully for this purpose is electrocoagulation (EC).

In its simplest form, an EC reactor may be made up of an electrolytic cell with one anode and one cathode [7]. When connected to an external power source, the anode material will electrochemically corrode due to oxidation, while the cathode will be subjected to passivation. A simple arrangement of an EC cell with an anode and a cathode in parallel arrangement is shown in Figure-1. A current is passed through a metal electrode (Aluminum in this work), oxidizing the metal (M) to its cation (M^{n+}), while water is reduced to hydrogen gas and the hydroxyl ion (OH^-), as can be seen in these equations:

$$M \rightarrow \qquad + \qquad\qquad\qquad\qquad \text{….. (1)}$$

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \qquad\qquad \text{….. (2)}$$
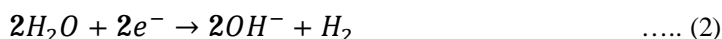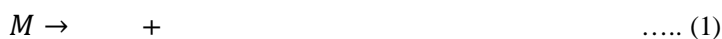
The theoretical amount of dissolved materials (m) can be calculated using Faraday's second law:

$$m = \frac{ItM}{nF} \qquad\qquad\qquad\qquad ..... (3)$$

Where n is the number of electrons transferred in the reaction at the electrode, M the molecular weight (g/mol), I is current flow and F is Faraday's constant (96,486 C/mol) and t is the time.

There are a variety of ways in which species can interact in solution, the inherent complexity of the process makes it difficult to model and control [8]. In brief three stages are developed in series in electrocoagulation. Initially the metal cations (Aluminum in this work) contribute to charge neutralization of the pollutant particles as the isoelectric point is attained. Here, a sorption coagulation mechanism occurs resulting in the formation of loose aggregates. As time progresses, further aluminum cation addition results in amorphous aluminum hydroxide precipitation that promotes pollutant aggregation via a sweep coagulation mechanism. During the final stages, coagulated aggregates interact with bubbles and float to the surface or settle to the bottom of the reactor [7].

Technologies for boron removal include conventional and advanced treatment technologies such as, chemical precipitation, ion exchange, reverse osmosis (RO), adsorption with Activated Carbon (AC), and Electro-dialysis (ED).

In chemical precipitation, there are several precipitants to be used for boron removal including metal salts such as the salts of calcium, magnesium, aluminum, manganese, iron(II), iron(III). Chemical precipitation could effectively remove boron but requires adjusting water pH to a high level, greater than 9. Therefore, this method causes high salinity and produces a voluminous amount of sludge for disposal. That cause a high costs for chemical demands and sludge disposal. These costs sometime prohibit the use of chemical precipitation for boron removal [9].
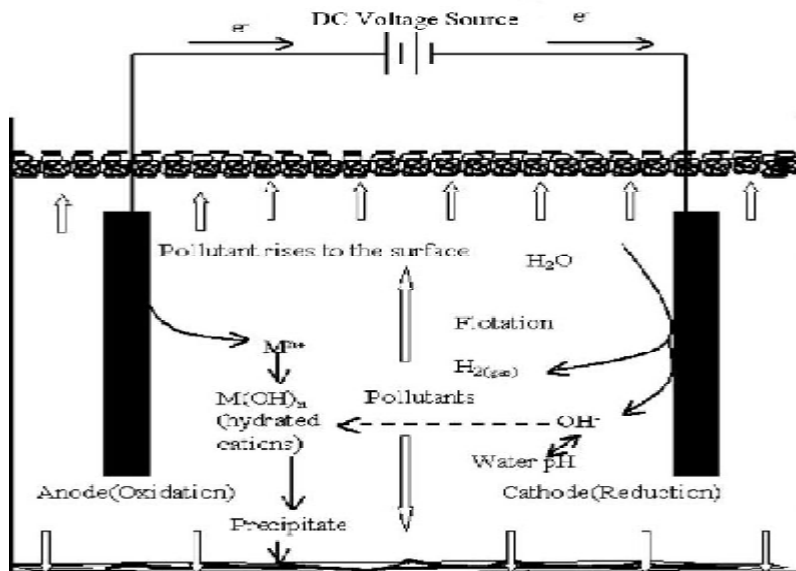

**Figure (1): Schematic diagram of a bench-scale two-electrode
electrocoagulation cell [7].**

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RO and ED are effective in removing boron from seawater for drinking water purpose. But there are disadvantages in these methods which are, producing brine water waste, the requirement of high pressures for multiple stages RO and thus high energy costs, raising pH greater than 11 results in the membrane scale/fouling problems, costly maintenance and replacement of membranes, and the need of full pretreatment process contribute significantly to total production cost [10]. Single stage SWRO membranes are able to reduce boron concentrations from sea water to about 0.9–1.8 mg/L in permeate. In some particular cases, however, even a two stage RO process working at normal operation conditions, is insufficient for reducing boron concentrations to the level that meets the drinking water quality requirements [11,12].

The principle of electrocoagulation was first patented in 1887 by Eugene Hermite [13]. He received two British and French patents which described a method of treating sewage by mixing with a proportion of seawater and electrolyzing. A treatment plant utilizing these patents was built in 1889 in London and operated for 10 years. In the same year, another plant for treating canal water was built in Salford, England. Iron electrodes were used and seawater added as a chlorine source for disinfection. In 1909, a patent for the purification of wastewater by electrolysis using aluminum and iron corroding electrodes was established in the USA [8]. Electrolytic sludge treatment plants were in operation as early as 1911 in Santa Monica, California and Oklahoma City. In 1925, the electrocoagulation of water purification with a soluble iron anode was first used at the Shature Power Station in the Soviet Union [13]. Mohammad and Muttucumaru published an excellent review for the application of EC to pollutant removal [14].

Iraq is one of the arid and semi-arid countries. For several years, Iraq has suffered from severe drought conditions. This leads to a significant reduction in surface water quantities and deterioration of its quality. As the level of fresh water flowing into Shatt al-Arab from the Euphrates and Tigris Rivers has declined, salty water from the Arabian Gulf has increasingly dispersed in it. This leads to increase the salt levels in several locations in Shatt-Alarab to high concentrations (TDS>10000 mg/l). Salt water flowing into the waterways renders the water unusable for agricultural purposes. Boron concentrations increased to reach a level of around 5 mg/l, which is 10 times the allowable content by WHO and by the Iraqi drinking water guideline [6].

MATERIALS AND METHODS

In this study, synthetic water with boron concentration of 5 mg/l was chosen because boron concentration from Shat al-Arab River water samples was about 5 mg/l. Electric conductivity of the water samples was adjusted by adding NaCl solution. The experiments were conducted in the Ministry of Science and Technology-Baghdad.

ELECTROCOAGULATION EXPERIMENTS

A laboratory-scale batch reactor (1 liter volume beaker), made of glass was used in electrocoagulation experiments. Aluminum electrodes, cathodes and anodes, were fixed vertically in the beaker. The two plates are identical and each with a surface area of 40 cm^2 and 1 mm thick. The net space between the electrodes was 5 mm. They were connected to terminals of a direct current power supply characterized by

the ranges 0–5A for current and 0–50V for voltage. Suspensions were stirred using a magnetic stirrer adjusted to an optimal rate (300 rpm) in order to attain the highest efficiency of turbidity removal [15]. Before the experiments, the electrodes were thoroughly cleaned and immersed in 1% HCl for 0.5 h [16].

At the beginning of each experiment the solution of boron of the desired concentration fed into the reactor. Each experiment was timed starting with the DC power supply switching on. Electrical conductivity, pH and temperature were all measured using a WTW multi-meter. Boron concentration was measured according to the standard method No. 4500B using the Curcumin method, while Aluminum concentration was measured according to the standard method No. 3500Al using Eriochrome Cyanine [4]. Electrocoagulation experiment setup is shown in Fig.-2.

Figure (2): Electro coagulation setup

CHEMICAL COAGULATION EXPERIMENTS

Chemical coagulation was evaluated using the standard jar testing technique, with three types of chemicals (Aluminum sulphate, Ferric chloride and Poly-Aluminum Chloride) as the chemical coagulants. NaOH and HCl solutions were added for any subsequent pH adjustment. Jar tests were performed using a six-paddle stirrer. Desired coagulant was added to boron-containing synthetic water in five different concentrations and leaving the sixth beaker as test control for comparison. Chemical dosages were (5, 10, 20, 35, and 50 mg/l). The procedures consisted of a 2 min rapid mix (120 rpm), 25 min slow mix (25 rpm), and a 30 min settling period (ASME D2035) [17]. After settling for 30 min, supernatants were collected to measure residual boron and pH values. All reagents used were of analytical grade.

RESULTS AND DISCUSSION
1- Effect of current density

In any electrocoagulation process current density (A/m^2, or mA/cm^2) and time of electrolysis are important operational parameters setting the ultimate removal and defining the electrical energy and power consumption, and thus the ultimate operating

cost for the process. The effects of current densities of (1, 3, 5 and 7 mA/cm^2) and operating time on boron removal percentage are shown in Figure-3.

For the applied range of current density, it was noticed that the boron removal efficiency keeps on increasing as current increases and as time increases. This was expected from Faraday's second law. After 30 min, the reduction rate becomes small and it will be costly to keep on the system runs after that. A time of 30 minutes was used by many other authors [14.15,16,18]. A current density of 5 mA/cm^2 has a good boron removal efficiency of 40% after 30 minutes operating time. This value was used in all other electrocoagulation experiments. Although, this value of current density came in consistence with other researchers [16,19], boron removal efficiency is lower than expectation.
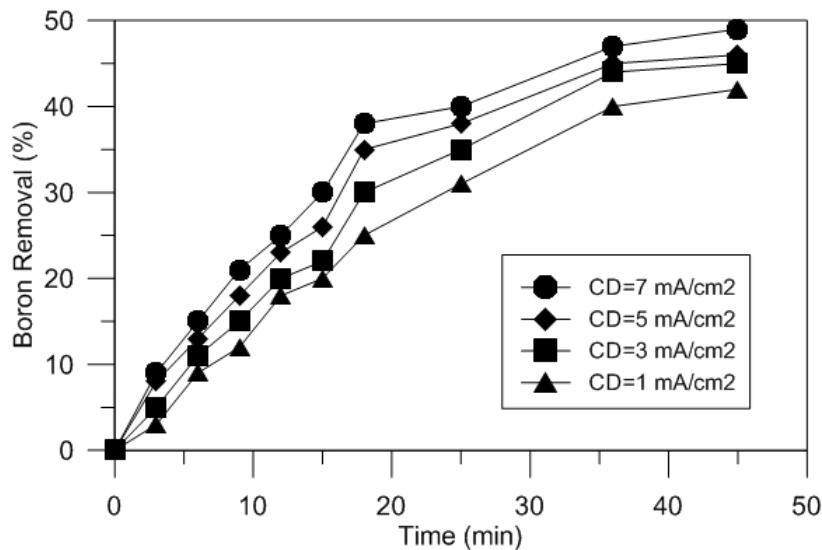

**Figure (3): The effect of current density and operating time
on boron removal percentages**

EFFECT OF INITIAL BORON CONCENTRATION

Initial boron concentration plays an important role in the treatment process using EC. Boron initial concentration is assumed to be in the range of (2-10) mg/l. The results of this experiment are shown in Figure-4. It is clear that Boron removal efficiency decreased with increasing boron concentration. This can be explained as follows; although the same amount Al^{+3} passed to solution at the same current density for all boron concentration, Al^{+3} was insufficient for solutions including higher boron concentration. This result came in consistence with other researchers [20]. Because of increasing boron concentration, the applied potential to the solution and the consumed energy was decreased as well.

Effect of initial pH

To examine the effect of initial pH, water samples are adjusted to the desired pH (3-10) for each experiment by adding sodium hydroxide or hydrochloric acid solution. The boron removal efficiency, as a function of pH, is shown in Figure-5. From this figure, it is clear that at pH of 8 there is a peak of boron removal efficiency and at the

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same time there is a significant reduction in dissolved aluminum concentration. If pH was higher (or lower) than 8, then the removal efficiency will drop significantly and aluminum concentration will goes high. Similar results were obtained by several authors [14,15,16,18].
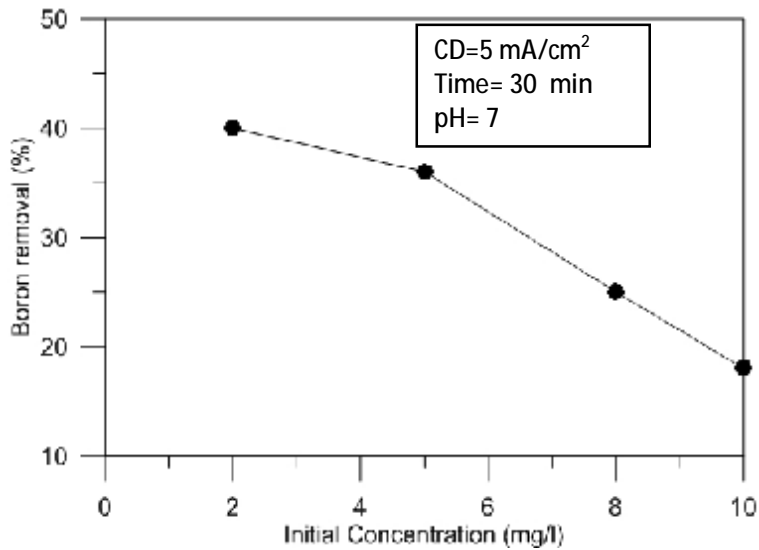

Figure (4): The effect of initial boron concentration
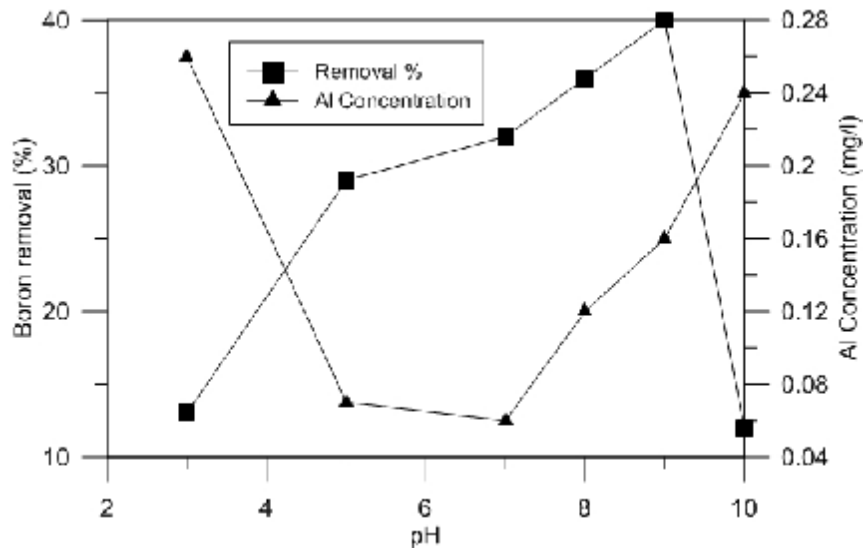**on boron removal percentages**

Figure (5): The effect of initial water pH on
Boron removal percentages

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Effect Of Water Conductivity

Surface water in Iraq has a broad variation in its conductivity ranging from few hundred (µS/cm) in the north to several tens of thousands in the south. Therefore, the effect of water conductivity in the range 1000-10,000 µS/cm on electrocoagulation in terms of boron removal was investigated. The results of this experiment are shown in Figure-6.

The greater conductivity will generally cause an increase in current density at the same cell voltage, or the cell voltage decreases with increasing water conductivity at a constant current density. So that, to fix the selected current density of 5 mA/cm^2, it was necessary to reduce the voltage of the DC power supply when testing higher conductivity. This has a significant effect on the power consumed in the treatment and accordingly the operating cost. Specific electric power consumption was calculated using simple ohm's law and it follows the same trend as voltage in this figure. Fortunately, consumed electric power is reduced as conductivity goes higher, which is the case in Shat Al-Arab. Moreover, the electrochemically generated chlorine is believed to be effective in water disinfections. From Figure-6, it was clear that Electrical conductivity had minor effect on the boron removal efficiency when the water product pH was kept constant. Small reduction was noticed due to the ions competition in capturing aluminum dissolved due to electrocoagulation.
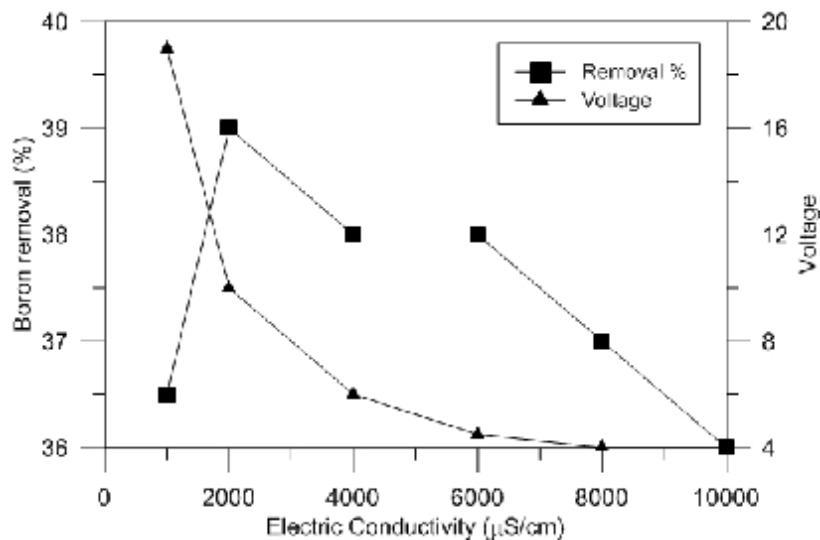

**Figure (6): The effect of initial water conductivity on
Boron removal percentages.**

Chemical Coagulation Experiments

Three test runs were conducted to evaluate the efficiency of Aluminum sulphate (Alum), Ferric chloride and Poly-Aluminum chloride to remove boron from synthetic water samples prepared in the laboratory with an initial boron concentration of 5 mg/l and turbidity of 25 NTU. Concentrations of chemical coagulants were varied from 5 to 50 mg/l. The results are shown in Figure-7.

From this figure, it is clear that PACl has a higher removal efficiency than both Ferric chloride and aluminum sulfate. However, along the applied dosage range, all the three coagulant showed low boron removal efficiency (max. 13%). This efficiency is very low and cannot be applied in the desalination pretreatment because boron concentration will not be changed much.

In order to enhance the PACl efficiency in removing boron, water pH was increased from 8 to 9. This will, theoretically, shift the boron in water toward the ionized borate forms. However, the results obtained in Figure-8 showed that Boron removal efficiency is even worse and reduced by about 70%. This is probably due to the effect pH on the solubility of aluminum ions in water.

Turbidity target of 5 NTU was achieved after a dosage of about 15 mg/l PACl. At this dosage, Boron removal percentage was 11% and 3% for pH of 8 and 9 respectively. These results came in consistent with other researchers [18].
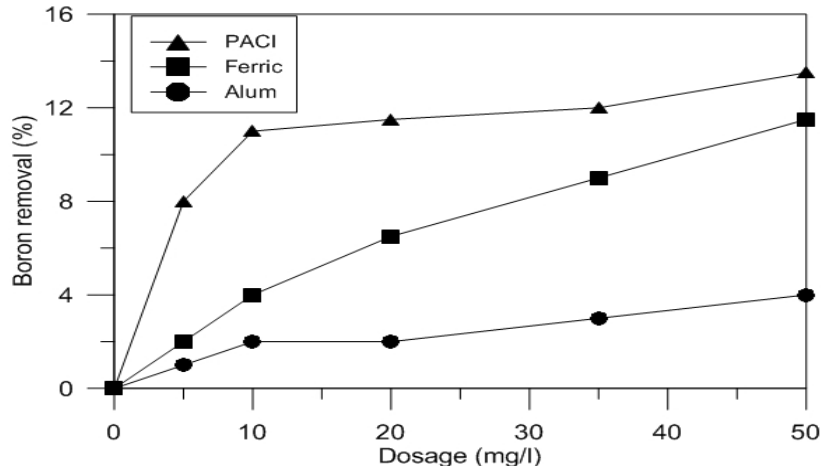

**Figure (7): Boron removal percentages with the dosage
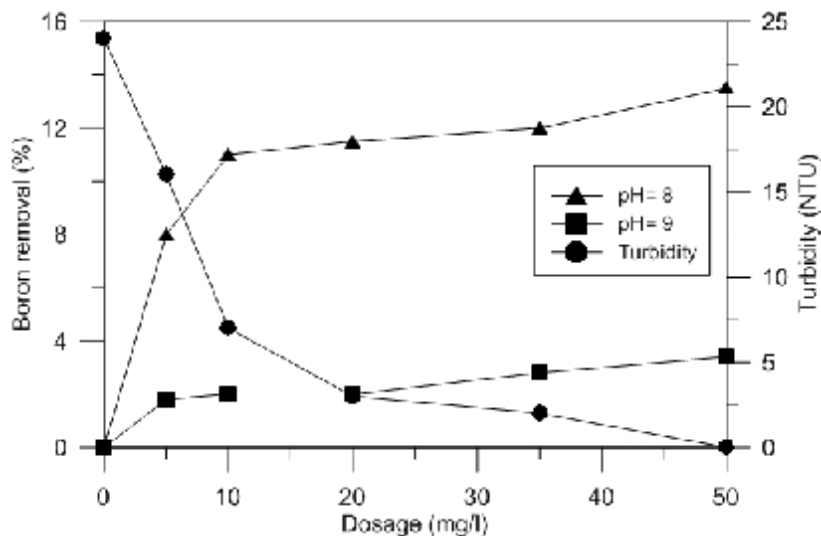of three chemical coagulants**

**Figure (8): Boron removal percentages and turbidity with
the dosage of PACl for pH of 8 and 9**

CONCLUSIONS

1- Chemical coagulation is not efficient to remove boron from surface water no matter what type and quantity of coagulants are used.

2- Electrocoagulation is a better technology to remove boron from surface water and it can be used as a pretreatment technology ahead of the existing RO desalination units in the south of Iraq to reduce the overall final boron concentration in the plants permeated water.

3- Boron removal efficiency obtained in this research was less than those published in the literature with similar operating parameters. Operation at current density of 5 mA/cm^2, time of 0.5 h and pH of 8 yields boron removal percentage of 40%.

4- Power consumption decreases with increasing water conductivity, which is the case in the south of Iraq. It is expected that the operation cost of the desalination units at such conditions will be about10%.

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