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Boron Removal from Aqueous Solutions Using Curcumin-Aided Electrocoagulation

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Abstract: This study seeks to find a new method to enhance the percentage of boron removed from aqueous solution by using the electrocoagulation process in the presence of curcumin. The optimum current density (CD), pH and dose of curcumin were determined as the operational parameters. The results showed that boron removal increased when CD was increased to 6.0 mA/cm^2 from 1.0 mA/cm^2. In our laboratory-scale reactor, the optimum pH and curcumin dose for the aqueous boron solution before electrocoagulation were 4.0 and 0.05 g, respectively. Electrocoagulation aided by curcumin removed was 20% more boron than the unaided electrocoagulation process.

Key words: Electrocoagulation · Boron · Curcumin

INTRODUCTION

Boron is normally presents in a very low concentration in soil and irrigation waters. Boron can also be found in industrial products such as fertilizers, insecticides, corrosion inhibitors in anti-freeze formulated for motor vehicle radiators and other cooling systems, pharmaceuticals and dyestuffs. These multiple sources have resulted in high amounts of boron compounds being discharged into the aqueous environment [1,2]. Because of the difficulties encountered in its removal, boron accumulates very rapidly in soils irrigated with wastewaters containing boron. Boron compounds passing into soil through surface and ground water combine and form many complex compounds with heavy metals, such as Pb, Cd, Cu and Ni. These boron compounds are even more toxic than the heavy metals that form them [3].

Boron is an essential element for healthy plants. Boron deficiency in plants may result in their reduced growth, loss of yield and even death, depending on the severity of the deficiency. When boron is deficient, plant stems and root apical meristems often die; root tips often become swollen and discoloured. Leaves will show various symptoms, including drying, thickening, distorting and wilting, in additional to chlorotic and necrotic spotting [4]. Although some plants need a small amount of boron as a nutrient, an excessive amount of boron can affect badly the growth of many agricultural products.

Boron's tendency to accumulate in vegetable tissues constitutes a potential hazard to the health of animals and humans consuming food and water with a high boron content [6]. In consequence, boron levels in drinking and irrigation waters are regulated. For human health, the World Health Organization (WHO) standard for the maximum boron level in drinking water is 0.3 mg/L [3]. To prevent the environmental problems arising from a high concentration of boron in waters, boron should be removed using one of several suitable methods [6], including precipitation by electrocoagulation and ion exchange [7-10].

Electrocoagulation is a process of creating metallic hydroxide flocks within the water by electrodissolution of the soluble anodes, usually made of iron or aluminium [11]. The difference between electrocoagulation and chemical coagulation is mainly in the way aluminium ions are delivered [12]. In electrocoagulation, coagulation and precipitation are not conducted by delivering chemicals called coagulants to the system, but via electrodes in the reactor [13].

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Electrocoagulation is based on the influence of ceated electric charges on the stability of colloids, suspensions and emulsions. If additional electrical charges are supplied to the charged particles in such a solution via appropriate electrodes, the surface charge of each particle is neutralized and several particles can combine into larger and separable agglomerates [14]. The electrode assembly is the heart of the treatment facility, therefore selecting appropriate materials is very important. The most common materials for the electrodes used in an electrocoagulation process are aluminium and iron. These materials are cheap, readily available and have been proven to be effective [15].

Curcumin is the principal c urcuminoid of the Indian curry spice turmeric. The other two curcuminoids are demethoxycurcumin and bis-demethoxycurcumin; these three curcuminoids are responsible for the yellow colour of turmeric. Curcumin is a polyphenol that can exist in at least two tautomeric forms, keto and enol. The enol form is more energetically stable in the solid phase and in solution [17]. It also has anti-tumour properties [18].

Curcumin can be used in the so-called curcumin method to quantify boron. The curcumin reacts with boric acid, forming a red-colored compound known as rosocyanine [19]. Rosocyanine is formed as a 2:1-complex from curcumin and boric acid in acidic solutions. Curcumin possesses a 1,3-diketone structure and therefore can be considered to be a chelating agent [27].

When boric acid ($H_3BO_{3)}$ and borates dissolve in water, they can form a number of different borate ions. The behaviour of the solution depends on a number of factors, including the concentration of boron, the temperature and the pH balance. The aim of this paper is to study the feasibility of removing boron from an aqueous solution using electrocoagulation aided by curcumin. The process was examined under different electric current density (CD), pH balance, time and concentration of curcumin.

Experimental Procedures: Boric acid powder (99.99% purity) and curcumin powder (99.99% purity) were purchased from Merck and Hach Companies, respectively. A solution of boron concentrated to 1000 mg/L was prepared by dissolving 5.88 g boric acid powder in a 1 L volumetric flask using sufficient volume of double-distilled water (ddH_2O) and then diluting to the mark with additional ddH_2O.

Table 1: Experimental parameters

Parameters	Range
pH	2, 4, 6, 8, 10and 12
Current density (mA/cm^2)	1, 2, 3 and 6
Curcumin dose (g)	0.005, 0.010, 0.050, 0.100 and 0.200

We studied the important parameters which affect boron removal, such as pH, CD and the dosage of curcumin. Table 1 summarizes the experimental parameters. All experiments were carried out at room temperature of 298 K.

A laboratory-scale reactor (16 cm × 10.5 cm × 10.5 cm) made of plexiglass was used in all experiments. Two groups of aluminium electrodes (eight cathode plates alternating with eight anode plates) were arranged vertically, with 1 cm spacing between the plates. The electrodes were connected to the terminals of an adjustable direct current power supply capable of delivering current of 0-6 A and voltage of 0-30 V

At the beginning of each test run, 1700 ml of the prepared boron solution, adjusted to the desired pH level for that test, was fed into the reactor along with the correct amount of curcumin for that trial and 15 mM $CaCl_2$ to maintain the conductivity of the boron solution. The solution in the electrocoagulation unit was constantly stirred at 150 rpm by a magnetic stirrer. Each run was timed starting when the direct current power supply was switched on and ending when the power was switched off. At the end of the trial, the contents of the reactor were emptied out for analysis. After each trial the reactor was flushed with ddH_2O.

The residual concentration of boron from each trial was measured potentiometrically by the Carmine method, using a DR/2400 spectrophotometer (Hach). The efficiency of removing boron by electrocoagulation, expressed as the percentage of the original boron load that was removed, was calculated as follows:

$$\eta\,(\%) = ([C_0 - C_e] / C_0) \text{ x } 100\% \quad (1)$$

where, η is the efficiency of removing boron, C_0 is the initial boron concentration and C_e is the boron concentration at equilibrium.

RESULTS AND DISCUSSION

The Effect of Adjusting the Ph Balance: The pH of the solution plays an important role in the electrochemical and chemical coagulation processes [20]. We examined the effect of pH on the boron removal at pH levels ranging

from 2 to 12. The CD and stirring speed were kept constant throughout the experiments at 3 mA/cm^2 and 150 rpm, respectively.

Boron removal increased as pH increased; the highest percentage removal was recorded at pH 4. Beyond pH 4, boron removal started to decrease; the lowest rate of removal occurred at pH 12.0. The change in boron removal at different pH depends on the hydrolysis and polymerization reaction of the dissolved Al^{3+} generated by the electrochemical dissolution of the aluminium electrodes. In the pH range of 4-9, $Al(OH)^{2+}$, $Al(OH)_2^+$ and $Al(OH)_3$ species are formed. The large positive charge on the surface of these compounds can stimulated the adsorption of boron through the electrochemical neutralization of the opposing charges between boron and the compound. At pH>10, the dominant species formed by dissolution of the electrodes is $Al(OH)_4$ and the coagulation effect rapidly decreases because $Al(OH)_4^-$ in dissolved form causes no flock formation. At a very low pH, boron removal was very low due to competition between the H_3O^+ ions from hydrolysis and the positively-charged ions from polymeric aluminium hydroxide [23].

The curcumin that is present in the acidic conditions during this experiment contributes to the boron removal process by forming rosocyanine. The formation of rosocyanine depends effectively on the reaction conditions, preferring acidic solutions containing hydrochloric or sulfuric acid [24].

Results indicated that boron removal also decreased when conditions were alkaline. When pH is enhanced, the surface of polymeric aluminium hydroxide will take on a negative charge. Since similar negative charges will cause a repulsion force, polymeric aluminium hydroxide no longer attracts $B(OH)_4^-$ [26].

The Effect of Changing the Current Density: The CD determines the coagulant dosage rate. Thus, CD should have a significant impact on how efficiently the process removes the boron. The results obtained are graphically illustrated in Fig. 2. Increasing the CD supplied increased the % B removal at which the Al electrode dissolved. Consequently, the rate of boron removal increased because at the higher CD, more Al^{3+} passed into the solution, increasing the rate at which $Al(OH)_3$ formed in the solution [6].

When CD increased, applied potential increased, as well. When CD was increased to 6.0 from 1 mA/cm^2, energy consumption also increased.

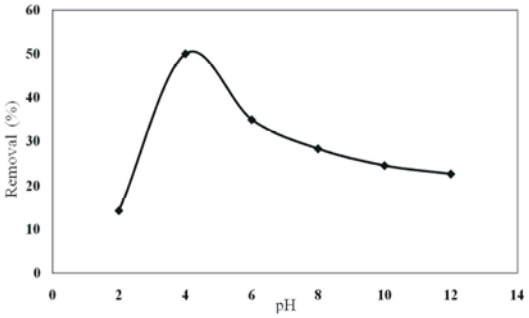

Fig. 1: The effect of pH on boron removal.

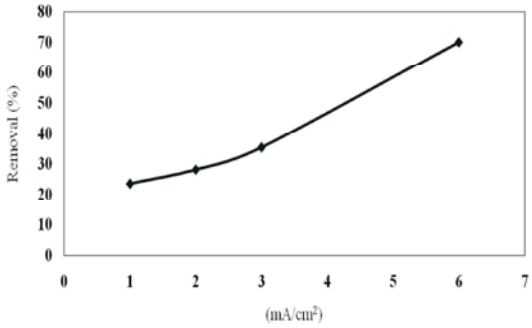

Fig. 2: The effect of current density on boron removal.

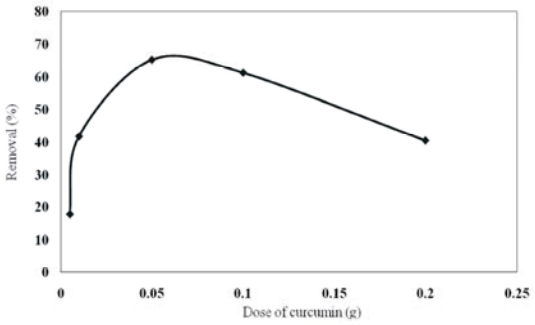

Fig. 3: The effect of the curcumin dose on boron removal.

The reactions that occurred at both sides of the electrodes can be described as follows [21]:

At the Anode:

$$Al_{(s)} \rightarrow Al_{(aq)}^{3+} + 3e^- \quad (2)$$

$$Al^{3+} + H_2O \rightarrow Al(OH)^{2+} + H^+ \quad (3)$$

$$Al(OH)^{2+} + H_2O \rightarrow Al(OH)_2^+ + H^+ \quad (4)$$

$$Al(OH)_2^+ + H_2O \rightarrow Al(OH)_3 + H^+ \quad (5)$$

$$Al(OH)_3 + H_2O \rightarrow Al(OH)_4^- + H^+ \quad (6)$$

At the Cathode:

$$2H_2O_{(l)} + 2e^- \rightarrow 2H_{2(g)} + 2OH^- \quad (7)$$

Fig 2 shows the possible further increase in the 5 removal of B by applying CD values higher than 6 mA/cm^2 ???

The Effect of Changing the Curcumin Dose: As shown in Fig. 3, as the curcumin dose increased to 0.050 g from 0.005 g, the percentage of boron removed by adsorption also increased, due to the larger surface area of available curcumin. Adsorption efficiency depends on the amount of adsorbent in the solution [25].

The adsorbent selected for this experiment is curcumin. The results showed that the optimum dose of curcumin is 0.050 g, which removed 65% of the boron. At a very low dosage of adsorbent, the surface of the adsorbent became saturated with metallic ions, leading to a small amount of adsorption. By increasing the adsorbent dose, removal of the metallic ions increased, due to greater availability of ion exchange sites [26].

Boron removal started to decline beyond a curcumin dose of 0.050 g. This decline may, reflect on increased competition from polymeric aluminium hydroxide, which also acts as an adsorbent through electrostatic forces. Boron adsorbs onto polymeric aluminium hydroxide more readily than onto curcumin. Dissolution of the electrodes produces these aluminium hydroxide complexes in the solution rapidly. This means that the aluminium hydroxide complexes become more effective in removing boron than curcumin, which depends on an acidic state to be effective.

Electrocoagulation Test: Two electrocoagulation experiments were carried out: one without curcumin and a second with curcumin. Both experiments applied all the optimum parameters determined previously: duration 75 min, CD supply 6 mA/cm^2 and pH 4. No curcumin was applied for the basic electrocoagulation experiment, while the optimum dose of 0.050 g of curcumin was added for the electrocoagulation experiment with the aid of curcumin.

Electrocoagulation Test Without Using of Curcumin: Theoretically, a simple electrocoagulation cell can be set up through a pair of electrodes, an anode and a cathode. When current is applied to the electrodes from a direct current (DC) generator, oxidation and reduction will take place at the anode and the cathode, respectively [21].

In this experiment, aluminium was selected as the electrode for both the anode and he cathode. Aluminium was used because the Al^{3+} ion that is produced by applying CD across the electrodes has a greater coagulation effect than the effect produced by other metals. In addition, Al metal is much cheaper and easier to use than other metals and its effectiveness in removing a pollutant has been proven [20].

The electrocoagulation process begins when Al is dissolved from the electrodes to form an Al^{3+} ion that reacts with the OH^- ion produced by the water hydrolysis process to form polymeric aluminium hydroxide. Various forms of monomeric cations such as $Al(OH)^{2+}$, $Al(OH)_2^+$ and $Al(OH)_4^-$ form, which later switch to $Al(OH)_3$ through a complex kinetic precipitation process [6]. These polymeric hydroxides are excellent coagulating agents.

The consumable (sacrificial) metal anodes continuously produce polymeric hydroxides in the vicinity of the anode. Coagulation occurs when these metal cations combine with the negatively charged particles carried towards the anode by electrophoretic motion. Contaminants present in the wastewater stream are treated either by chemical reactions and precipitation or by physical and chemical attachment to colloidal materials generated by the electrode erosion. These contaminants are then removed by electroflotation, sedimentation and filtration. In a conventional coagulation process, coagulating chemicals are added. By contrast, in the electrocoagulation process, these coagulating agents are generated in situ.

In a parallel reaction, water is electrolyzed, producing small bubbles of oxygen at the anode and of hydrogen at the cathode. These bubbles attract the flocculated particles from the pollutants and float them to the surface through natural buoyancy [21].

The coagulation process started when cationic species merged with negatively charged particles in solution, such as boron ($B(OH)_4^-$), through electrophoretic motion. Pollutants which are present in this solution will be treated either through chemical reaction and precipitation or fixed chemically or physically in colloid particles that are generated through electrode dissolution. Hydrogen gas production also plays an important role in the mixing process and in producing flock. The H_2 bubble ties up flock particles and lifts them to the surface of the solution [21].

Electrocoagulation Test with the Aid of Curcumin: In this experiment, curcumin was added during the electrocoagulation process to observe the effect of various dosages of curcumin on the percentage of boron removed.

Curcumin is a classic reagent which has been used to detect boron. The colour reaction between borates and curcumin is used in the spectrophotometric determination and quantification of the amount of boron present in food or materials. Rosocyanine and rubrocurcumin are two red-colored materials formed by the reaction between curcumin and borates [27].

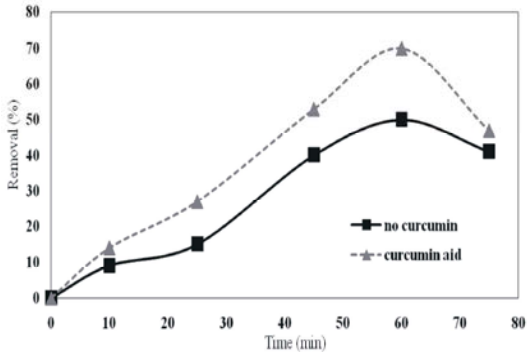

Fig. 4: Electrocoagulation test on boron removal with and without the aid of curcumin.

The formation of rosocyanine depends on the reaction conditions. Preferably, the reaction is carried out in acidic solutions containing hydrochloric or sulfuric acid. The colour reaction can also take place under different conditions, but in an alkaline solution, gradual decomposition is observed. At higher pH values, the reaction might be disturbed by interference from other compounds [22].

Curcumin was used as the adsorbent in our experiments to react with the boron in the solution and form rosocyanine complexes. Rosocyanine is formed from curcumin and boric acid in acidic solutions as a 2:1-complex. Curcumin possesses a 1,3-diketone structure and can therefore be considered as a chelating agent [19].

In these experiments, curcumin-aided electrocoagulation removed a maximum of 70% percent of the boron, a 20% increase compared to unaided electrocoagulation, which only removed about 50% of the boron at peak efficiency. Fig. 4 shows that the increase in the percentage of boron removed by the adsorption process aided by curcumin peaked at the same duration of time during the electrocoagulation process as the unaided process.

CONCLUSION

This study showed that electrocoagulation with the aid of curcumin could be applied effectively in the treatment of industrial wastewater containing boron. The use of curcumin as an adsorbent material in the treatment of boron wastewater by electrocoagulation was found to be pH dependent. The most effective removal of boron was achieved at pH 4. The boron removal rate increased monotonically with increasing the CD, within the range of our experiment. The highest CD resulted in the fastest treatment time for removing a given quantity of boron.

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