

# ELECTROCHEMICAL pH CONTROL IN HYDROPONIC SYSTEMS

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## Abstract

This paper reports an innovative method based on electrochemistry to adjust the pH in nutrient solutions used in hydroponics. The required quantity of  $H^+$  or  $OH^-$  ions is produced in-situ through electrolytic water decomposition. Because the direction and rate of electrochemical reactions can be easily manipulated by controlling the polarity and voltage applied between electrodes, the most important advantage of this method in comparison to traditional pH control using chemicals is the possibility to accomplish accurate and reliable pH control to within a narrow, preset pH range. Moreover, additional positive effects of improving the quality of added raw water such as alkalinity control, reducing the concentration of sodium, and water disinfection can be accomplished in the same electrolytic unit. Electrochemical technology offers possibilities to eliminate the risk of pH control failures due to overdoses and excludes the necessity of having reagent (acid and base) storage tanks and of handling these hazardous materials. Important savings of reagents, dosage and mixing equipment, storage tanks and improved environment and safety objectives can be realized. Available greenhouse space can be used more efficiently.

## 1. Introduction

The pH of plant root environment is an important factor affecting the uptake of many nutrients. The optimum range for many crops lies between 4.5 and 6.0 (Voogt, 1995) - a narrow range near neutrality. Water used for hydroponic plant production must first be brought to the proper pH range. This principally involves using acids to treat for bicarbonate content. After initial pH adjustment of the source water to within the proper range, plant root activities continuously modify the pH of the nutrient solution of a hydroponic plant production system. The most conspicuous action is the release of an  $OH^-$  ion for every nitrate ( $NO_3^-$ ) ion that is taken up (to maintain charge neutrality within the plant). The resulting continuous increase of nutrient solution pH must be counteracted by continuous (or frequent) addition of acid. Acid injection requires care and timing and the solution must be thoroughly mixed to prevent localized concentrations of a strongly acidic solution. If plant roots are exposed to a low pH (for example, a pH of 2 - 3) for only a few seconds, immediate damage can result.

Controlling pH to within a narrow range near neutrality is considered to be a very difficult problem. When concentrated alkali or acid is used, even a small overdose causes

large pH changes. Use of dilute alkali and acid requires large storage tanks. If traditional pH control is to work, special attention must be paid to the design and installation of electrodes, transmitters, controllers, control valve(s), piping, and mixing equipment. A mistake in the design or installation of any component can cause the control system to fail (McMillan, 1994).

This paper reports aspects of an alternative method based on electrochemistry to adjust pH in nutrient solutions used in hydroponics. The required quantity of  $H^+$  or  $OH^-$  ions can be produced in-situ through a process of electrolytic water decomposition. Because the direction and rate of electrochemical reactions can be easily manipulated by controlling the polarity and voltage applied between electrodes, the most important advantage of this method in comparison with traditional pH control using chemicals is the possibility to accomplish accurate and reliable pH control within a narrow (preset) pH range. Moreover, electrochemical technology offers possibilities to eliminate the risk of pH control failures due to overdoses and exclude the necessity of having reagent (acid and base) storage tanks with the need to handle these hazardous materials. Thus important savings (reagents, dosage and mixing equipment, storage tanks) and improved environment and safety objectives can be realized.

The purpose of this study was to evaluate, experimentally and theoretically, the most important characteristics of pH control electrotechnology such as specific productivity of an electrolytic unit working as an acid/base generator; capacity (or acid-base availability) in make up water which can be electrochemically exploited; and specific quantities of electricity (and energy) needed to control the alkalinity level and pH in water and hydroponic nutrient solution. Theoretical research was focused also on developing a simulation model for an electrochemical pH and alkalinity control unit and, using this model, to evaluate system characteristics for different scale-up applications.

## 2. Fundamentals of electrochemical pH control

Electrochemical pH control is based on electrical decomposition of water in an electrolytic cell divided by an ion-exchange membrane or diaphragm into anode and cathode compartments. The minimum (theoretical) voltage necessary to decompose water is 1.23 V at 25 °C. Actual decomposition voltage is higher because of the irreversible nature of electrodes. A visible evolution of gases ( $O_2$  and  $H_2$ ) commences at 1.7 V (Regner A., 1957). At a chemically inert anode, water decomposition takes place according to the reaction:



The cathode reaction of water decomposition is:

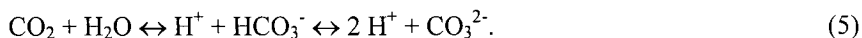


Thus, the anodic reaction (1) can be exploited to reduce the pH of an aqueous solution and, concomitantly, the cathodic reaction (2) to raise pH. By applying 1 F (96500 C) of electricity at the anode, 1 mol of hydrogen (acid) ions will be generated and, at the cathode, 1 mol of hydroxyl (base) ions. (Note, in this report, F symbolizes Faraday and C symbolizes Coulomb). At the same time 1 gram equivalent of ions will pass through the membrane via electrical migration. The quantity of specific ions transferred through the membrane is determined by their transference numbers (Rogov, 1989).

Usually either the anodic or the cathodic reaction should be employed for pH control, while the complementary reaction may be undesired in some practical applications. As the case may be, a more suitable complementary reaction can be selected. For example, if the evolution of hydrogen must be avoided as the cathode reaction, an option may be one of the following reactions:



Weak bases or acids dissolved in water may significantly influence pH control. For electrochemical pH control in hydroponics, as well as with traditional pH control techniques, the carbonate buffering system is very important through the reactions



### 3. Integrating an electrochemical pH control unit into a hydroponic system

Diagrams in Figure 1 illustrate several possible arrangements for electrolytic control of pH in hydroponic nutrient solutions. The principal  $\text{H}^+/\text{OH}^-$  producing electrode(s) may be immersed directly into the nutrient solution (Figure 1A), the recirculating nutrient solution circuit (Figure 1B), or the water being supplied to the nutrient solution tank (Figure 1C). The opposite electrode should be immersed in a separate chamber (half-cell) with an electrolyte, which is in electrical contact with the nutrient solution through a diaphragm or an ion exchange membrane. By employing a cation exchange membrane, passage of ions through the membrane can be limited to all or only monovalent cations. Using an anion-exchange membrane and a compact  $\text{Cu}/\text{CuSO}_4$  complementary half-cell may be very attractive for some pH control applications. When considering which of these embodiments is most suitable for a specific hydroponic application, one should evaluate, first, the impact that electrolytic pH control may have on the nutrient solution formulation over the entire plant growth period.

Hydroponic plant growth is mostly an acid consuming process, thus electrolytic pH adjustment will be associated with the transfer of cations ( $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ , etc.) from the nutrient solution through a cation exchange membrane into the auxiliary electrolysis vessel by electrical migration. In the case with an  $\text{Cu}/\text{CuSO}_4$  complementary electrolysis vessel and an anion exchange membrane as the partition wall,  $\text{SO}_4^{2-}$  ions will be transferred through the membrane into the nutrient solution. The quantity of nutrients transferred by electrical migration through the membrane will be proportional to the quantity of  $\text{H}^+$  ions required to maintain the desired pH level in the root-zone environment.

There will be no adverse impact of the electrolysis process on nutrient concentrations in the hydroponic system when  $\text{H}^+$  ions are generated in the water being supplied to the nutrient solution tank (Figure 1C). Furthermore, additional positive effects of improving the quality of make-up water, such as alkalinity control, reducing the sodium level, and water disinfection can be accomplished in the same electrolytic unit. The questions to be answered first in this approach are:

How much acid or base can be produced electrolytically in supplied water?

Will this quantity suffice to substitute completely for the traditional method of adding chemicals to control alkalinity in the supply water and pH in the nutrient solution?

How much electrical energy will be consumed for electrochemical pH control?

### 4. Limits of electrochemical pH control of water

The pH of water can be modified electrochemically over a wide range (Rogov, 1989). For pH control it is important to evaluate, first, the maximum concentration limits of base and acid that can be produced in a given water sample. The limits are determined by the kinds and concentrations of all elements dissolved in the water. It is possible, using electricity, to produce water with any content of base or acid within these limits.

In terms of capacity to neutralize acids, bicarbonate ions contained naturally in water act as base. For example, 1 mol of  $\text{HCO}_3^-$  ions will neutralize 1 mol of  $\text{H}^+$  ions, and *vice*

*versa*. Thus, untreated raw water is actually a basic solution with an equivalent concentration of base (as mmol l<sup>-1</sup> of OH<sup>-</sup>) equal to the content of bicarbonate ions in the water. Using the anodic reaction (1), the alkalinity in water can be controlled accurately by generating the quantity of H<sup>+</sup> ions required to effect bicarbonate decomposition through



After alkalinity removal is completed, continued electrolysis will increase the concentration of free H<sup>+</sup> ions in water. The maximum (theoretical) concentration of H<sup>+</sup> ions in the anode compartment water may reach the value equal to the concentration of all anions, except HCO<sub>3</sub><sup>-</sup>. Thus, for many sources of natural water,

$$[\text{H}^+]_{\text{max}} = 1/2 [\text{SO}_4^{2-}] + [\text{Cl}^-]. \quad (7)$$

Correspondingly, the lowest pH value in samples of natural water that can be obtained by treating it in an anode compartment can be evaluated as

$$\text{pH}_{\text{min}} = -\log(1/2 [\text{SO}_4^{2-}] + [\text{Cl}^-]). \quad (8)$$

The electrolytic process of reducing the alkalinity level of water and increasing its acidity is illustrated in Figure 2. The evolution of pH values during the electrolysis of water in the anode compartment is shown for three samples of water. The kinds and concentrations of anions contained in these water samples are presented in table 1. Thus, for tap water in Ithaca, NY, USA, only about 120 C l<sup>-1</sup> of electricity is needed to neutralize the alkalinity while, for river Reut water (Moldova), the point of zero alkalinity is reached after consuming approximately 700 C l<sup>-1</sup> of electricity. The pH of the same water samples after treatment with 1500 C l<sup>-1</sup> will reach 2.9 and 2.4, respectively. Although these values are rather close, the difference in acid concentration in treated samples is quite significant. The estimated base capacity in untreated water and maximum acid capacity in anodically treated water are presented in Table 1. These data show that the acid-base capacity of most natural water which could be exploited electrolytically for the purpose of pH control in hydroponics is rather high. This makes it possible to reduce significantly or even to avoid the use of additional acid and base in many horticultural applications.

## 5. Results and discussion

An experimental evaluation of electrochemical pH control in a NFT hydroponic unit for butterhead lettuce (having a growing area of 12 m<sup>2</sup>) was performed during November-December, 1996. Half-strength standard nutrient solution and reverse osmosis (RO) water were used. The recirculating nutrient solution was directed to pass through the anode compartment of a small electrolytic apparatus. A cation exchange membrane was used as a partition wall between the anode compartment and the cathode compartment. The desired pH range of 5.6-6.0 was maintained by adjusting manually the voltage applied to the electrolytic unit in response to data obtained from pH measurements. The voltage applied was varied in the range of 2.5-6 V. The corresponding current values ranged from 10 to 80 mA, or about 50 mA as average value during 24 days of plant growth. For a NFT leaf lettuce growing area of 100 m<sup>2</sup> electrical power of approximately 5 W will be needed for electrochemical pH control, which is a rather modest consumption of electrical energy.

In order to estimate the performances of the electrochemical pH control method for other horticultural applications and the impact it may have on nutrient solution formulation, we have developed a simulation model. Some results derived from modeling the electrolytic pH control are presented in Table 2. These data are related to the

arrangements shown in Figures 1A, B when a  $H^+$  producing electrode is immersed directly into the nutrient solution. The figures illustrate the relationship between the quantity of  $H^+$  ions that should be electrolytically supplied to keep the preset pH value of the nutrient solution and the concentrations of main nutrients affected during the electrolysis by electrical migration of ions. Considering, for this example the standard nutrient solution for tomatoes (Voogt, 1997) it follows that the level of  $K^+$  will decrease by 7.7 %, of  $Ca^{2+}$  by 11 % and of  $Mg^{2+}$  by 10 %, correspondingly, for each mmol of  $H^+$  produced when electrolysis is performed through a cation exchange membrane. When an anion exchange membrane and Cu/CuSO<sub>4</sub> half cell are employed only the  $SO_4^{2-}$  concentration is affected. For each mmol of  $H^+$  generated at the anode, 0.5 mmol of  $SO_4^{2-}$  ions will migrate through the membrane into the nutrient solution.

Generating the required quantity of  $H^+$  ions electrolytically in make-up water supplied to the nutrient solution tank (Figure 1C) consume more electrical energy because of the lower electrical conductivity (EC) of raw water as compared with the EC of commonly used hydroponic nutrient solutions. Nevertheless this approach may be the most suitable for many hydroponic applications because there is no potential adverse impact of the electrolysis process on nutrient concentrations in the hydroponic system. Furthermore, in addition to controlling pH and the alkalinity level, additional improvements in supply water quality may be achieved such as reducing the concentration of minerals dissolved in water (TDS); selectively removing sodium as an undesirable element in source water; saturating the water with oxygen; water disinfection, removal of certain inorganic and organic pollutants. A significant quantity of CO<sub>2</sub> is continuously produced as by product in the process of water dealkalizing, which is an important factor for plant growth. The electrochemical approach to pH and alkalinity control makes successful hydroponic plant production possible in areas with high levels of alkalinity in natural waters and situations where adding acid may be excessively costly.

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Table 1. The concentrations of anions and estimated acid/base capacity in some water sources, determining the limits for electrochemical pH control

Water Sources	Concentration of anions in water, ppm			Base capacity of raw water, mmol/l as OH <sup>-</sup>	Acid capacity of treated water, mmol/l as H <sup>+</sup>
	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>		
1. Tap water (Ithaca, NY, USA)	104	12	25	1.7	1.0
2. Nistru River (Moldova)	195	84	71	3.2	3.75
3. Reut River (Moldova)	479	476	135	7.8	13.6

Table 2. Data illustrating the impact of pH control on the nutrient solution formulation depending on the quantity of H<sup>+</sup> ions to be generated electrolytically into the nutrient solution in order to maintain the preset pH value

The ion-exchange membrane employed in the pH control unit and main parameters of the nutrient solution affected during electrolysis	Quantity of H <sup>+</sup> ions to be generated electrolytically into the nutrient solution in order to maintain the present pH, mmol/l					
	0	1	2	3	4	5
1. Cation-exchange membrane:						
K <sup>+</sup> , mmol/l	6.5	6	5.5	5	4.5	4
% of depletion	0	7.7	15.4	23	31	42
Ca <sup>++</sup> , mmol/l	2.7	2.4	2.1	1.8	1.5	1.2
% of depletion	0	11	21	32	42	51
Mg <sup>++</sup> , mmol/l	1.0	0.9	0.8	0.7	0.6	0.5
% of depletion	0	10	20	30	40	50
2. Anion-exchange membrane and Cu/CuSO <sub>4</sub> half cell:						
SO <sub>4</sub> <sup>2-</sup> , mmol/l	1.5	2	2.5	3	3.5	4
% extra input (build up)	0	33	67	100	133	167

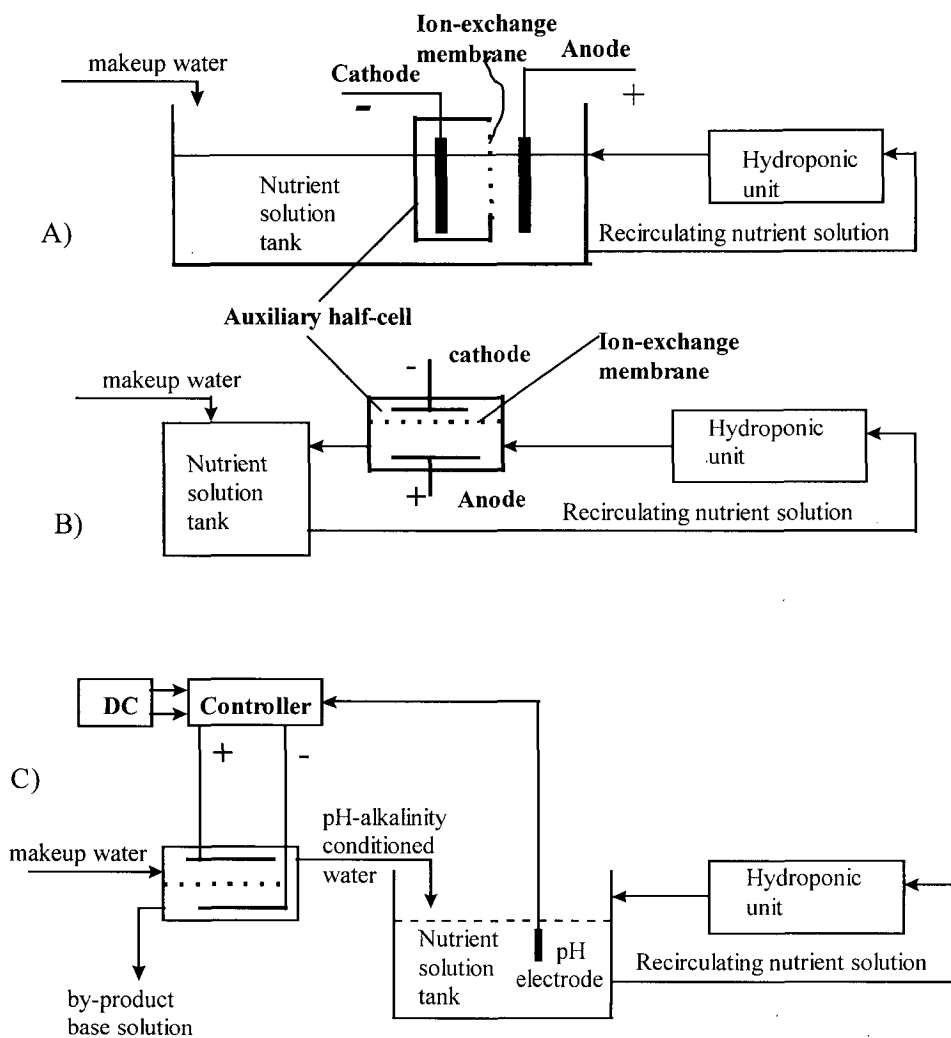


Fig. 1. Diagrams illustrating some approaches of integrating an electrolytical pH control apparatus in a hydroponic unit: A) in the nutrient solution tank; B) in the recirculating nutrient solution circuit; C) in the supply water line.

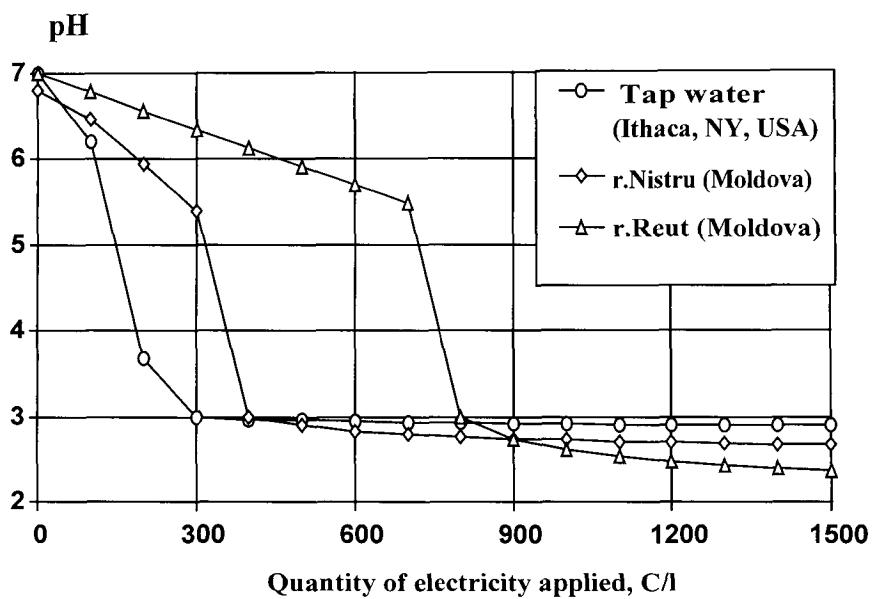


Figure 2: The evolution of the pH of water during the electrochemical treatment in the anode compartment of samples from different water sources