

## Determination of the Point of Zero Charge for Electrocoagulation Precipitates from an Iron Anode

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This study determined the variation of current, temperature, pH, and amount of precipitate generated during an electrocoagulation process conducted using a pure iron electrode in 0.1 Na<sub>2</sub>SO<sub>4</sub>. Then, the points of zero charge of the hydroxide/oxyhydroxide precipitates thus produced were obtained by two different methods: a simplified mass potentiometric titration method and a salt titration method. The results from both methods yielded *pzc* values of  $3.6 \pm 0.7$ . This signals the predominance of positively-charged surface groups. Users desiring the removal of specifically-charged water pollutants can use this information to adjust the pH values for such purposes.

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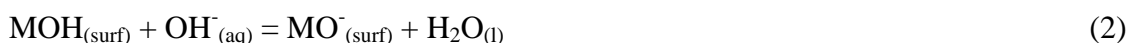
**Keywords:** electrocoagulation, sludge, oxyhydroxides, point of zero charge, *pzc*

### 1. INTRODUCTION

Adsorption of water pollutants on solid particles with their subsequent removal is a very effective method for the cleanup of various types of wastewaters. Colloidal particles are especially ubiquitous as pollutants, and their wide-ranging sizes preclude a single type of treatment based either on physical or chemical principles. Coagulation is commonly a fitting choice for this purpose. Here, a highly charged polyvalent cation is added (typically from Fe(III) or Al(III) chlorides or sulfates) to neutralize the negatively charged surfaces of suspended particles. In doing so, interactions among particles can be activated with their ensuing agglomeration and coagulation.

In order to prevent the concomitant addition of anions in the coagulation step, the electrical route offers the *electrocoagulation* process (EC) as an alternative [1-12]. Here, Fe or Al anodes are used in an electrochemical cell to furnish the corresponding Fe<sup>n+</sup> or Al<sup>3+</sup> ions required for the

coagulation process. When such ions encounter the hydroxyl ions produced by water electrolysis at the cathode of the cell, iron hydroxide/oxyhydroxide precipitates form. These were first reported by us to be attracted to a magnet, thus facilitating their physical removal [13]. Understandably, this attraction depends on the magnetic nature of the Fe(II) or Fe(III) species. Since these precipitates adsorb many types of pollutants out of an aqueous matrix, we set out to analyze the amounts of these species produced. Upon contact with water, these precipitates acquire a surface charge that controls to a large extent their interfacial behavior [14]. This charge stems from the dissociation of functional surface groups and corresponds to a preferential accumulation of charged species at the interface. If the surface species are symbolized as  $\text{MOH}_{(\text{surf})}$  the following processes are clearly dependent on the concentration of  $\text{H}^+_{(\text{aq})}$  or  $\text{OH}^-_{(\text{aq})}$ :



Such amphoteric behavior allows the surface of each precipitate particle to develop either a positive or negative overall electrical charge. Alternatively these reactions can be visualized as deprotonations:

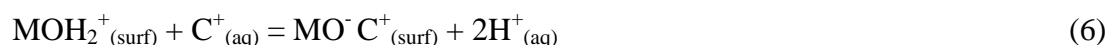


If the concentrations of the two types of sites resulting from equations 1 and 2 (or 3 and 4) are the same, there is no net charge on the surface. This condition is called the *point of zero proton charge*, *pzpc* (or *zero proton condition*, *zpc*). At solution pH values lower than that required for attaining the *pzpc*, the sites become protonated and an excess positive charge develops on the surface (the oxide behaves as a Brønsted acid and as an anion exchanger). The contrary occurs at pH values higher than the *pzpc*, where the oxide behaves as a Brønsted base and as a cation exchanger. Mixed oxides can have both exchange types, depending on the relative  $\text{p}K_a$  values of the different surface sites [15, 16].

The *pzpc* can thus be measured by potentiometric titration if  $\text{H}^+$  and  $\text{OH}^-$  are the only aqueous ions involved. In practice, however, electrolytes typically contain other anions,  $\text{A}^-$  and cations,  $\text{C}^+$  that may adsorb onto the surface sites as follows:



and/or



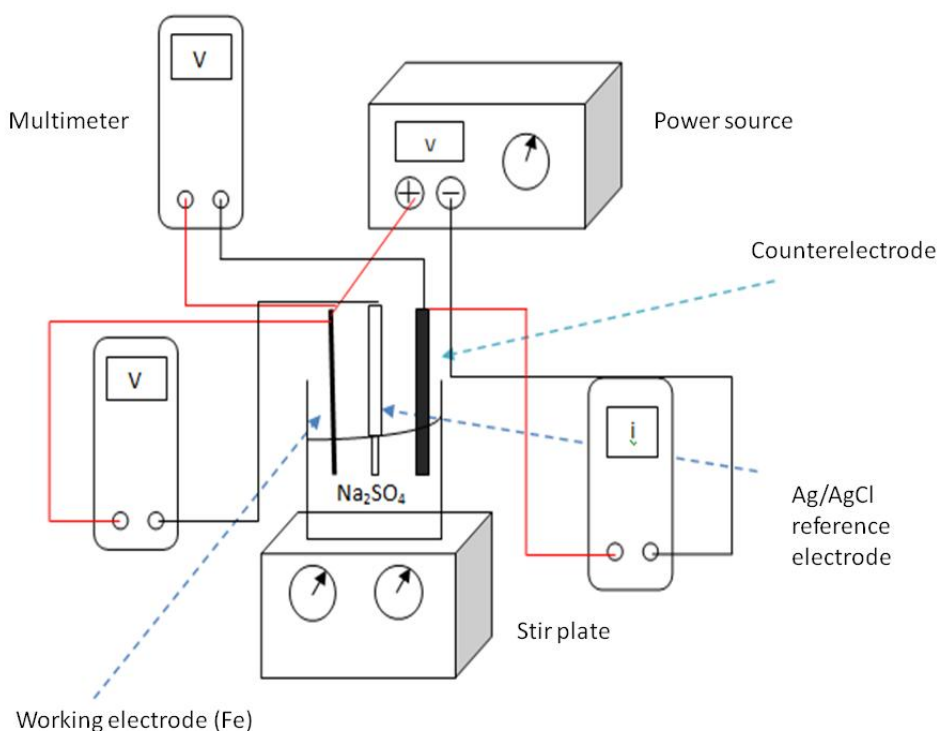
In these cases the net surface charge not only depends on the  $H^+$  and  $OH^-$  ions in the medium, but also on the concentration of the electrolyte (that provides  $A^-_{(aq)}$ ,  $C^+_{(aq)}$ ). The pH of the aqueous solution at which the sum of the all the surface positive charges balances the sum of all the surface negative charges is called the *point of zero charge*,  $pzc$ . In the absence of sorbed ions other than protons, the  $pzpc$  is clearly equal to the  $pzc$ . Due to inhomogeneities that can develop in certain suspensions, the  $pzc$  values measured for the same solid may vary widely [14, 16, 17-19]. In the present paper we report the  $pzc$  values obtained by a simplified mass potentiometric titration method and by a salt addition method for a series of electrocoagulation precipitates. These parameters are of paramount importance for the present purpose since at pH values higher than the  $pzc$ , positively-charged species may adsorb (e.g., cationic dyes) on the particle, whereas the opposite is true at pH values lower than the  $pzc$ .

## 2. EXPERIMENTAL

EC precipitates (sludge) were produced and their  $pzc$  values determined as follows.

### 2.1. Production of EC precipitates

The electrochemical system is described elsewhere [13] and consisted of a Teflon capped 5-mL glass conical bottom vial ( $\phi = 1.5$  cm, 3 cm high) with a typical 3-electrode arrangement.



**Figure 1.** Experimental arrangement.

The anode was a Fe wire (Aldrich,  $\phi = 0.5$  mm, 99.9% pure), the cathode was a graphite rod (Staedtler,  $\phi = 2$  mm), and the reference was a Ag/AgCl electrode (Bioanalytical Systems, BASi MF-2052). The supporting electrolyte was a 0.1 M NaSO<sub>4</sub> solution (J. T. Baker) purposefully non deaerated so as to mimic real conditions more pragmatically. The Fe electrode was submerged in 5 % v/v HNO<sub>3</sub> for 1 min to eliminate the natural passivated layer and then rinsed with deionized water to remove any acid remains. The three electrodes penetrated into the cell through appropriate holes in the Teflon cap (so as to have a 1 cm length immersed in the solution) and they were placed 1 cm apart from each other. An external DC potential was applied (nominal values of 3, 5, 8, 10 and 15 V) during 3 min with a TES-6100 power source (capacity = 30 V). The resulting precipitates were then allowed to dry in air and further dried in a Fisher Scientific oven at 70 °C. Voltage and current were monitored with TES-2310 hand held multimeters (connected in parallel or in series, respectively). See Figure 1. All the EC experiments were performed in triplicate. Deionized water was used throughout all the experimentation and the analytical reagents were used as received.

## 2.2. Spectrophotometric analysis

Each sample (i.e., liquid + precipitate) resulting from the EC experiments was transferred to a 10-mL volumetric flask to which 0.1 mL of conc. H<sub>2</sub>SO<sub>4</sub> (J. T. Baker, ACS reagent) was added to dissolve the hydroxide/oxyhydroxide precipitate. 1.0 mL of a 0.25 % (w/w) *o*-phenanthroline (Merck, 99.5 %) solution in 1/100 (v/v) H<sub>2</sub>SO<sub>4</sub> was added to produce analytically suitable iron complexes [20]. 2.0 mL of 0.2 M sodium acetate solution (J. T. Baker, ACS reagent) was also added to control the pH and prevent the dissociation of the complexes. The resulting mixtures were brought to the 10-mL mark with deionized water.

Aliquots were taken into a 1.0 cm path length quartz optical cell and their absorbances were measured in a 2000 USB Ocean Optics spectrophotometer at 510 and 390 nm for the Fe<sup>2+</sup> and Fe<sup>3+</sup> determinations respectively, previous preparation of a calibration plot described elsewhere [13]. The concentrations in mg/L were then calculated from the resulting linear fit.

## 2.3. *pzc* determination

The *pzc* value was determined for each precipitate generated at the different values of applied external potential as follows.

### a) Simplified mass potentiometric titration method [14, 16]

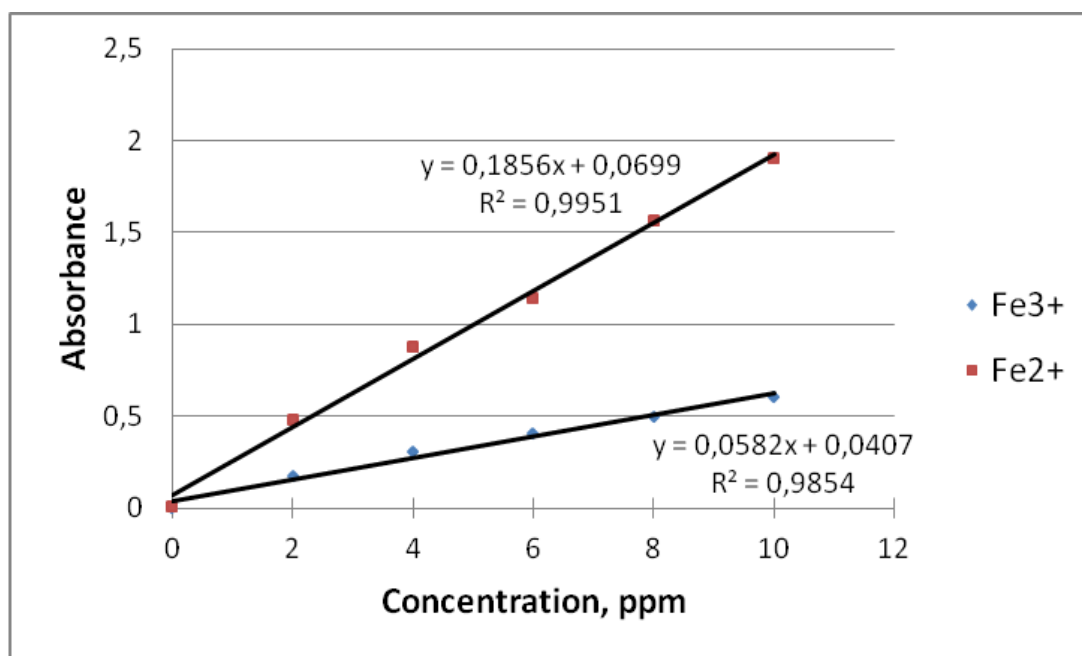
Two identical solutions (*blank* and *sample*) were prepared with 3.0 mL of 0.1 M KNO<sub>3</sub> and 6.0 mL of deionized water, and their pH values were measured with a Conductronic 120 pH meter. 1.0 mL of 0.01 M KOH was added to the *blank* solution and the pH measured again. 50 mg of the EC precipitate was then added to the *sample* solution, followed by 1.0 mL of 0.01 M KOH. Both the *blank* and the *sample* were then titrated with 0.01 M HNO<sub>3</sub> and the results were plotted. The *pzc* of each sample was estimated at the point where both titration curves crossed.

### b) Salt addition method [17]

This consists of a simple titration that requires a smaller amount of solid sample than other methods [17]. Here, 0.200 g of each EC precipitate was added to 40.0 mL of 0.1 M NaNO<sub>3</sub> in ten 50-mL plastic beakers. The pH was adjusted using a ThermoElectron Orion 4 Star pH meter to 2, 3, 4, 5, 6, 7, 8, 9, 10 and 11 ( $\pm 0.1$  pH units) with 0.1 M HNO<sub>3</sub> and 0.1 M NaOH as needed in each beaker. These were then shaken for 24 h in a revolving water bath to reach equilibrium (Gyratory water bath shaker G76). After this time each resulting pH was measured and the initial pH (pH<sub>0</sub>) vs. the difference between the initial and final pH values ( $\Delta pH$ ) was plotted. The *pzc* was taken as the point where  $\Delta pH = 0$ .

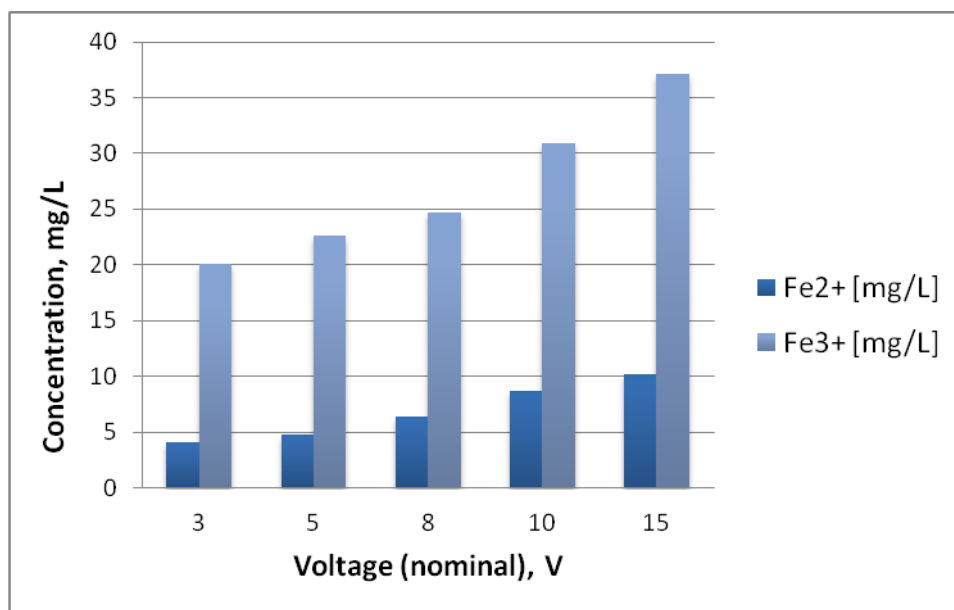
### 3. RESULTS AND DISCUSSION

The calibration curve resulting from the application of the procedure in ref. [20] to the determination of Fe(II) and Fe(III) allowed the simultaneous quantization of both oxidation states and is given in Figure 2.



**Figure 2.** Calibration curves for Fe<sup>2+</sup> and Fe<sup>3+</sup>.

Then, the Fe<sup>2+</sup> and Fe<sup>3+</sup> concentrations in the solutions containing the dissolved EC precipitates were evaluated. Results are given in Figure 3. In all cases, Fe<sup>3+</sup> was more abundant than Fe<sup>2+</sup> in a ratio between 3.5 and 5 to 1. This Fe<sup>3+</sup> predominance facilitates the magnetically-assisted removal recently proposed by us [13].



**Figure 3.** Fe<sup>2+</sup> and Fe<sup>3+</sup> concentrations at different applied potentials. Each point is the average of three determinations.

As mentioned earlier, the nominal applied potentials were 3, 5, 8, 10 and 15 V. The measured cell and electrode potentials are given in Table 1. Potentials at the anode remained essentially constant throughout the experiment.

**Table 1.** Nominal (cell), measured (cell), and anodic potentials.

E <sub>cell</sub> (nominal), V	E <sub>cell</sub> (measured), V	E <sub>anode</sub> vs. Ag/AgCl Initial (t = 0), V	E <sub>anode</sub> vs. Ag/AgCl Final (t = 180 s), V
3	3.12	1.03	0.95
5	5.24	2.53	2.33
8	8.11	4.60	4.50
10	10.1	5.37	5.20
15	15.07	10.13	9.97

In order to better characterize the system, the current, solution temperature, solution pH, and amount of precipitate produced were also monitored. Current increased with time in all the experiments, especially in those at the higher voltages (Figure 4). This is likely a result of at least two factors: a) the temperature elevation (of up to 6 °C) observed in Figure 5, as this increases ionic mobility, and b) the cathodic production of OH<sup>-</sup> evidenced by the pH increase shown in Figure 6. (The anodic current is known to be fundamentally used for the oxidation of Fe.) The amount of precipitate produced increases with the higher currents derived from the application of higher applied voltages, as it would be expected for a Faradaic process (Figure 7).

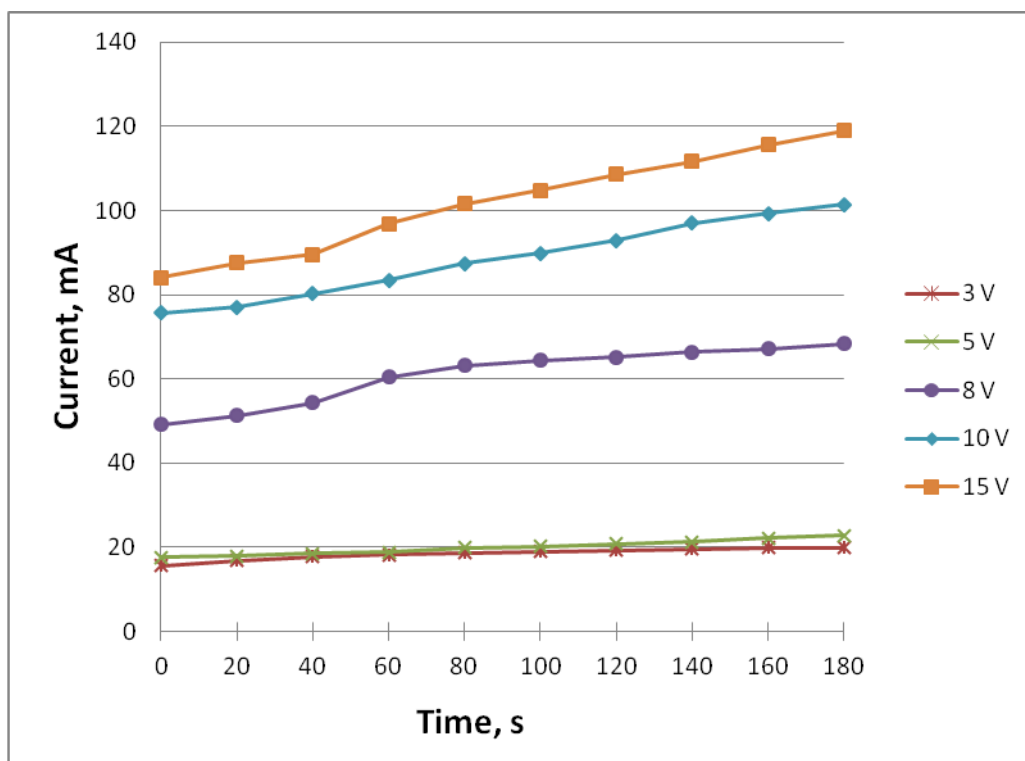


Figure 4. Variation of current with time.

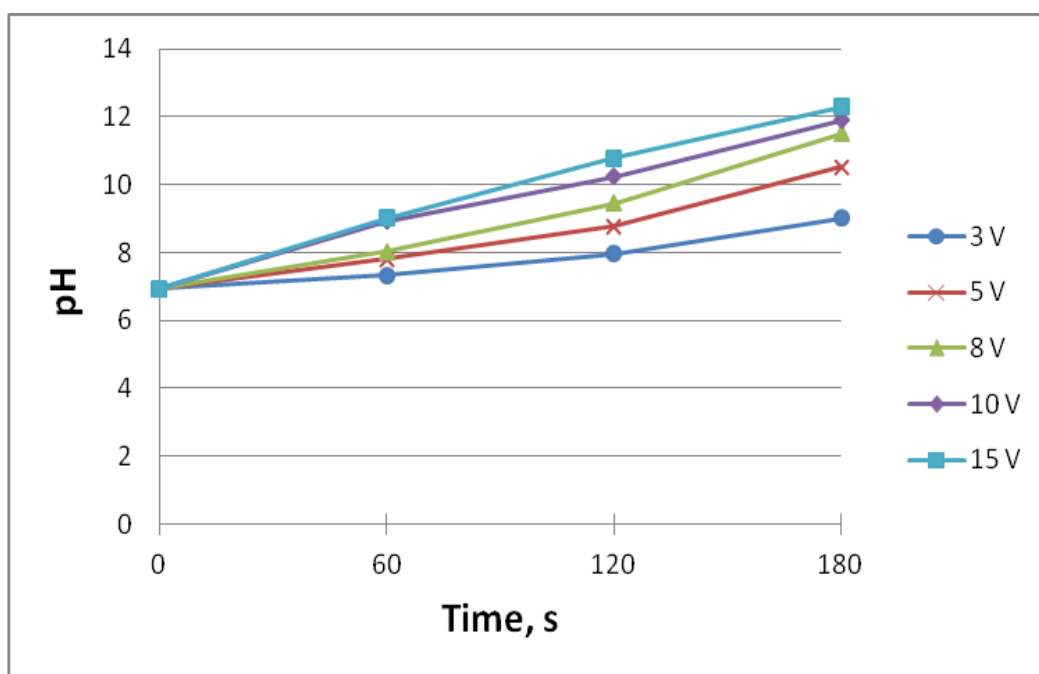


Figure 5. Variation of pH with time.

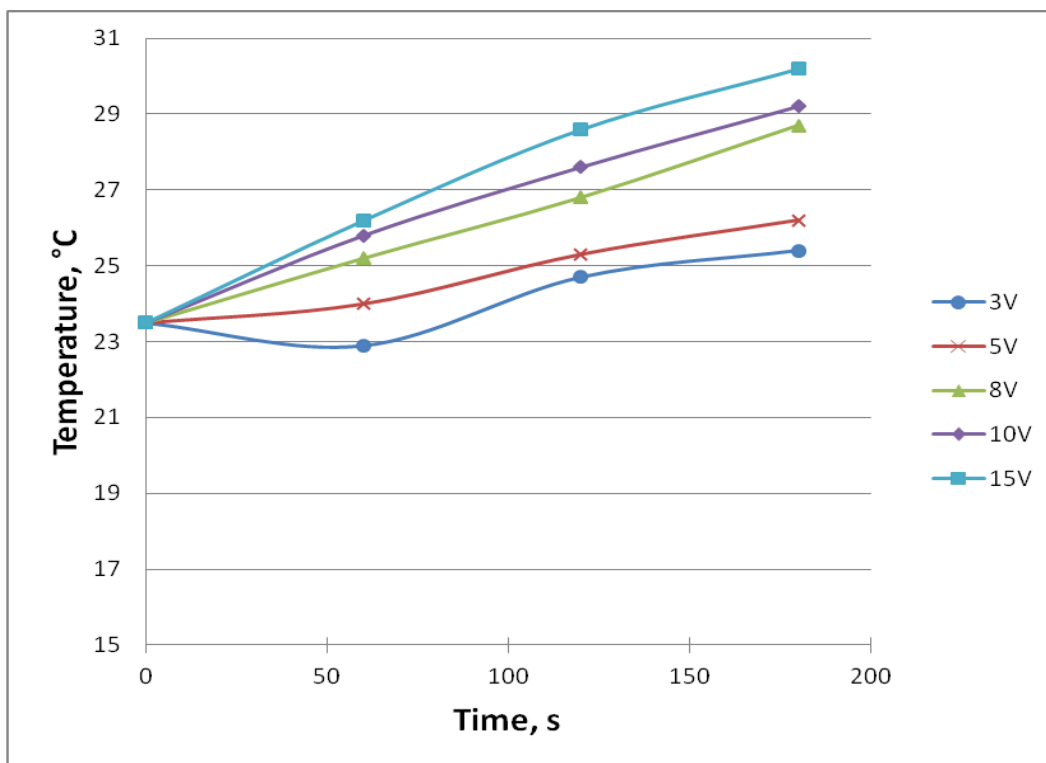


Figure 6. Variation of temperature with time.

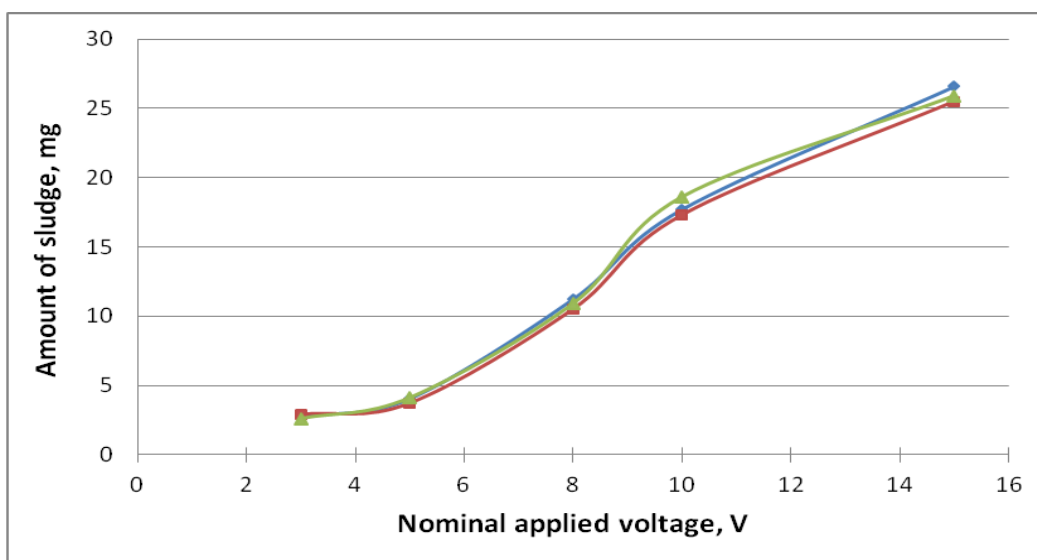


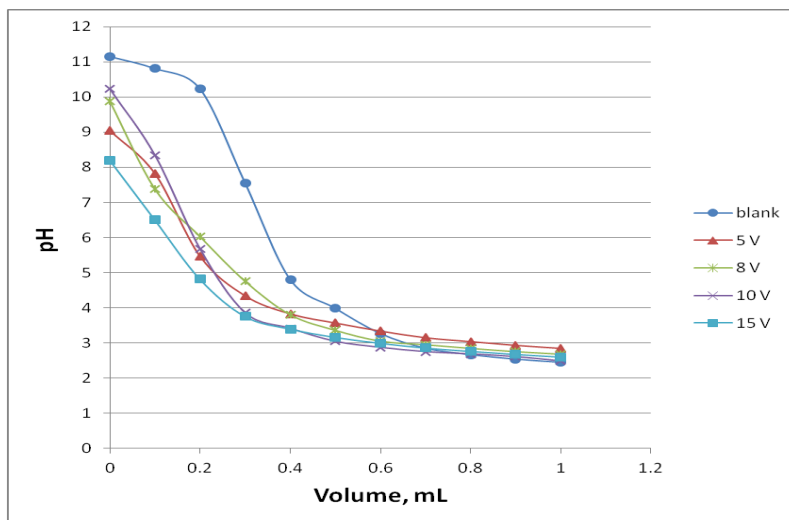
Figure 7. Amount of precipitate (sludge) produced as a function of the nominal applied voltage (triplicate experiments).

### 3.1. Simplified mass potentiometric titration method

To obtain the *pzc* using this method, the EC precipitates were titrated as described earlier. The *pzc* values were estimated from the curve interceptions (Figure 8) and are summarized in Table 2.



(Note that the amount of precipitate obtained at the nominal applied potential of 3 V, shown in Figure 7, was not sufficient for the *pzc* experiments).

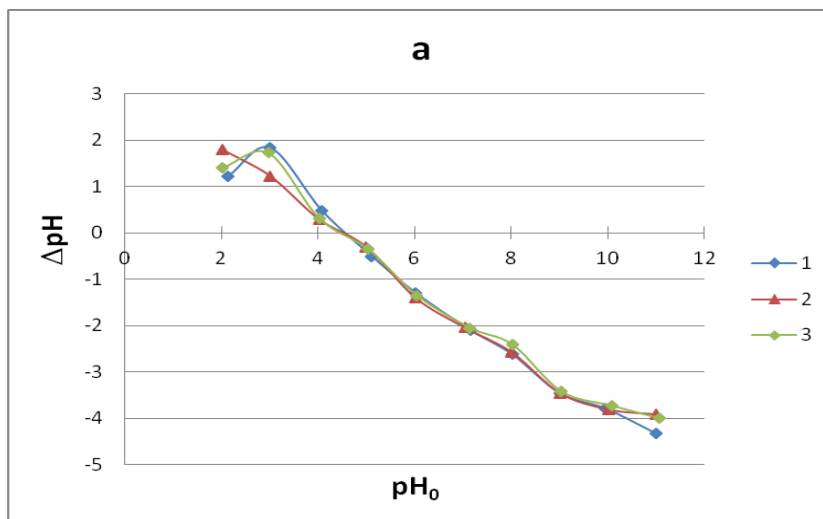


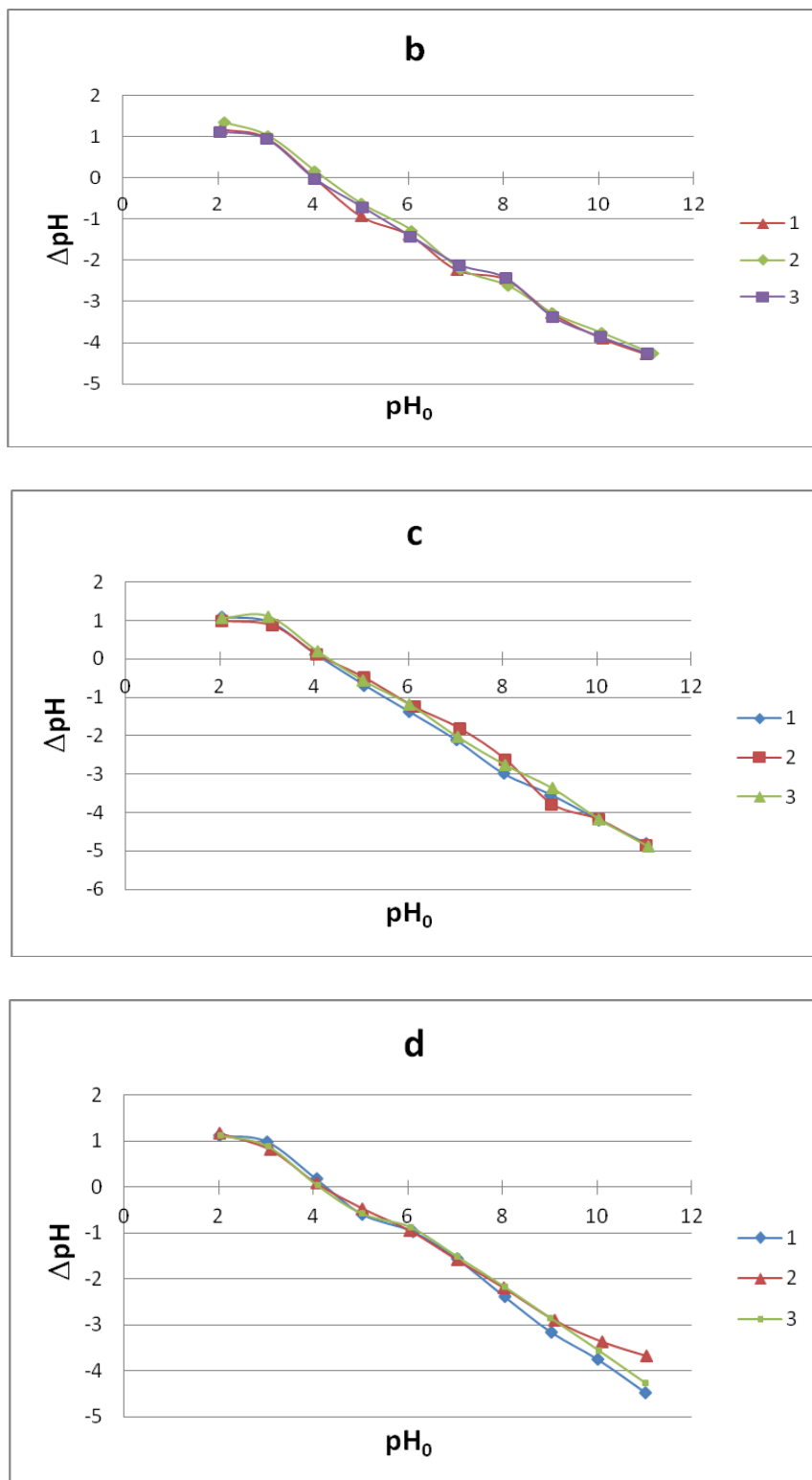
**Figure 8.** *Pzc* determination with titration curves of the blank solution and of the suspensions containing the EC precipitates obtained at different voltages.

**Table 2.** Experimental *pzc* values for triplicate experiments ( $\sigma$  = std. dev.).

Nominal voltage, [V]	<i>pzc</i> ± $\sigma$
5	3.4 ± 0.2
8	3.0 ± 0.3
10	2.8 ± 0.2
15	2.8 ± 0.2

3.2. Salt addition method





**Figure 9.**  $pH_0$  vs.  $\Delta pH$  using the salt addition method. Electrocoagulation precipitate obtained at: a) 5 V, b) 8 V, c) 10 V, and d) 15 V. Triplicate experiments are shown.

The value obtained at the intersection of the initial pH ( $pH_o$ , x-axis) with the  $\Delta pH = 0$  line (y-axis) in Figure 9 gives the  $pzc$  of the suspended solid. The  $pzc$  for the precipitates obtained at different applied voltages are summarized in Table 3.

**Table 3.** Experimental values of  $pzc$  (salt addition method). Results of triplicate experiments.

Nominal voltage, [V]	$pzc \pm \sigma$
5	$4.5 \pm 0.1$
8	$4.1 \pm 0.1$
10	$4.2 \pm 0.1$
15	$4.2 \pm 0.1$

The results shown in Tables 2 and 3 are self-consistent. They give an overall average of  $3.6 \pm 0.7$ , which is an acceptable standard deviation for such a varied range of chemical compositions of the hydroxide/oxyhydroxide precipitates analyzed earlier [16]. This relatively low  $pzc$  value signals the predominance of positively-charged surface groups. It is noteworthy that in both methods the precipitates obtained at higher voltages tend to display lower  $pzc$  values, signaling a higher concentration of positively-charged groups than in those obtained at the lower voltages. With this, information users desiring positive or negative surface charges to remove specific pollutants shall be able to adjust their pH values accordingly.

#### 4. CONCLUSIONS

The current, temperature, and pH increased with time, while the amount of precipitate increased with the applied potential during an electrocoagulation process in a cell using an iron anode and a synthetic  $\text{Na}_2\text{SO}_4$  electrolyte. The points of zero charge of the hydroxide/oxyhydroxide precipitates thus produced were obtained by two different methods and their results were self-consistent. These values are in the range of  $3.6 \pm 0.7$ , which shows a predominance of positively-charged surface groups. Users desiring the removal of specifically-charged water pollutants shall be able to use this information to adjust the pH values for their purposes.

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