Electrocoagulation: Clarification of Residual Water From Chemistry Laboratories

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Abstract: This paper adresses the application of the electrochemical method to the treatment of chemical residues in the analysis and research laboratories in the areas of chemistry at Instituto Federal de Educação, Ciência e Tecnologia do Amazonas — IFAM, whose main objective was the removal of pollutants without adding chemicals. The acrylic reactor with a capacity of 40 L was divided into three tanks of 0.29 m high by 0.20 m long and 0.262 m wide (15.2 L per unit), with a ½ in. pipe for the waste inlet and outlet of treated water. The residues from the laboratory of physicochemical analysis — called residues 1, 2 and 3 — were characterized with analyzes of pH, conductivity, turbidity, alkalinity, COD and solids. The electrochemical cell was assembled with monopolar electrodes in parallel with an arrangement of 2 pairs of honeycomb electrodes, using a solid aluminum plate with a thickness of 3 mm and 200 mm high by 200 mm long, cut in one corner of each plate diagonally in order to place the fixing screw, with 400 cm² submerged in the residue. The direct current source was "Fonte de Alimentação ICEL Manaus PS-3005", with output voltage from 0 to 32 Volts, amp from 0 to 5A, input voltage of 110-220 Volts, without polarity inversion. Currents from 3A to 5A were used, depending on the chemical properties of the residue, with a reaction rate of 2 to 4 hours. The plates (sacrifice electrodes) were weighed before and after the electrocoagulation/flocculation with a 5.7g mass loss. The pH and alkalinity showed an increase after the reaction for all residues, with a decrease in turbidity and color. The washout of the pollutant varied according to the increase in pH and the compounds formed with $Al(OH)_3$. In view of the results obtained in the experiments and analyzing the acceptable limits for legal disposal, issued by CONAMA Resolution 403/2011, it can be inferred that the system is efficient and removes most of the dissolved or suspended substances from the liquid effluents of the teaching and research laboratories.

Key words: residues from the IFAM chemical laboratory, electrocoagulation system

1. Introduction

The generation of chemical residues in the analysis and research laboratories in the areas of chemistry and biology is quantitatively lower when compared to large industries in the same field, such as chemicals and petrochemicals. The big problem with this form of generation is the varied and inconsistent composition of residues, as they constantly change and it is difficult to find a standard and effective method for their treatment.

In techniques based on electrochemistry, in which coagulation reactions take place inside a reactor with metallic electrodes, resulting in the dissolution of this metal with the generation of ions and gases (hydrogen and oxygen), the contaminants present in the residual water stream are treated both by chemical reactions and precipitation or physical and chemical bonding to colloidal materials that are being generated by the erosion of the electrode. They are then removed by electroflotation, or sedimentation and filtration.

The electrocoagulation process is used in various industrial effluents to remove chemical and food waste and sanitary sewage. According to Theodoro, 2010, "it is a versatile technique with easy operation and no cost with chemical reagents, it appears as an alternative to

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carry out oxidation and not only transfer the phase of interest, but to aggregate the particles in the solution in an aqueous medium for removal of the pollutant by electroflotation".

Khandegar and Saroha, 2013, point out the main advantages of electrocoagulation in relation to conventional chemical coagulation: no need to add chemicals and better removal capacity for the same species, startup time is minimal, less sludge production and consequently lower costs to dispose of this material, in addition, the generated sludge is more easily filterable and can be used as an additive for the soil. However, the technique also has some limitations, such as the need to periodically replace the sacrificial anodes, requires minimal conductivity of the solution, the possibility of forming an impermeable oxide film on the cathode that can cause resistance to the flow of electric current and also the high cost of electricity, which can result in an increase in the operational cost of EC [1].

The work was developed for the residues of the chemical laboratories, mainly the physical-chemical laboratory, where the flow of analyzes and experiments is greater and had as main objective to clarify the liquid effluents of the laboratories by removing color and turbidity first with the consequent removal of the main pollutant compounds in a simple batch, by electrocoagulation/electrofloculation.

2. Methodology

The project was developed at IFAM-CMC, with the following steps: assembly of the electrochemical reactor, characterization of the effluents from the DQA/IFAM/CMC physicochemical laboratories, reaction in the batch reactor, analyzes of the reactor effluent.

2.1 Assembly of the Electrochemical Reactor

The acrylic reactor with a capacity of 40 L was divided into three tanks of 0.29 m high by 0.20 m long and 0.262 m wide (15.2 L per unit), with a ½ in. pipe

for the waste inlet and outlet of treated water, Fig. 1, with the aim of treating residues from different laboratories simultaneously.

The electrochemical cell was assembled with monopolar electrodes in parallel with an arrangement of 2 pairs of honeycomb electrodes, using a solid aluminum plate with a thickness of 3 mm and 200 mm high by 200 mm long, cut in one corner of each plate diagonally in order to place the fixing screw. In the center the plates are drilled with a 10 mm hole for fixing a central PVC screw. The distance between the electrodes was 30 mm, Fig. 2.

The direct current source was "Fonte de Alimentação ICEL Manaus PS – 3005", with output voltage from 0 to 32 Volts, amp from 0 to 5A, input voltage of 110-220 Volts, without polarity inversion.

2.2 Characterization of the Effluents of the Physical Chemistry Laboratories of DQA/IFAM/CMC

The residues from the practical classes in the
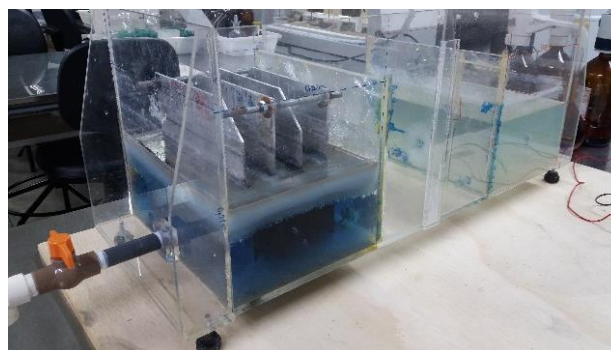

Fig. 1   Acrylic reactor with the electrochemical cell in the first tank.

Fig. 2   Assembly of the electrode plates of the electrochemical reactor tank.

physico-chemical and analytical laboratory were collected and separated into four types of residues. They were stored in 20 L barrels, generating an approximate total volume of 80 L of chemical residues, with distinct characteristics of color, pH, turbidity and conductivity.

In order to better characterize the residues, a mapping of the various analytical procedures that generate liquid residues was carried out by analyzing the scripts of the practical classes in the chemistry laboratories. It specifies the chemical composition of the effluent.

Several authors have observed that the pH, color, turbidity and conductivity of the affluent to the electroflotation reactor is an important operational factor that influences the performance of the electrochemical process [2].

Table 1 shows the four types of residues collected on different dates and practical classes and therefore characterizes the chemical compositions. Residue 1 has a variety of alkali metal and alkaline earth metals salts, transition metals, organic and inorganic acids. Residue 2 has transition metal salts, such as sulphate and nitrate salts, inorganic acids, as well as a cobalt complex. Residues 3 and 4 are similar, but there is a lesser diversity of salts and the presence of nickel salts in the residue.

The identified residues were submitted to analytical methodologies based on the Standard Methods of Water and Wastewater [3]. The parameters analyzed were pH, turbidity, conductivity, chemical oxygen demand (COD), alkalinity, chlorides.

2.3 Electrocoagulation Reaction in the Batch Reactor

The residues were subjected to the electrocoagulation and electroflocculation process in a batch electrochemical reactor with currents of 3 to 5 A, time of 2 to 4 h, with polarity inversion every 30 minutes.

Electrocoagulation transformed the impurities into "solid" flakes, forming two distinct phases: treated

Table 1   Chemical composition of liquid residues from the physico-chemical and analytical laboratories.

Residues	Chemical composition of practical classes: Analytical and inorganic chemistry
1	Acetic acid 1 mol/L, NaOH 1 mol/L
	Phenolphthalein and methylorange indicators, Bromocresol green Alkaline earth metals
	Determination of H_2O_2
	Copper Salts. $BaCl_2$, $CaCO_3$
	$AgNO_3$; 0.101 mol/L, NaCl, $K_2Cr_2O_7$, H_2SO_4, 0.1 mol/LHCl $AgNO_3$; 0.1012 mol/L, NaCl, $K_2Cr_2O_7$, 1 mol/L H_2SO_4, 1mol/L HCl
2	H_2SO_4. Ag_2SO_4
	$CuSO_4$
	$Cu(NO_3)_2$
	HCl, HNO_3, $Hg(NO_3)_2$
	$CuSO_4.5H_2O$, Soybean oil
	Cobalt Complex $[Co(NH_3)_5 CNO]Cl$
	$K_2Cr_2O_7$, K_2CrO_4
	$FeCl_3$
3	Acetic acid 1 mol/L, HCl mol/L
	Sodium chloride NaCl 1 mol/L
	HCl 1.0 mol/L, H_3PO_4 1 mol/L H_2SO_4 H_2O_2 10 V
	Nickel Complex $[Ni(H_2O)_6] Cl_2$

liquid effluent and solid residue (treatment sludge), separated by flotation/sedimentation and filtration. The liquid effluent was subjected to the same analytical methodologies by which the initial residue was analyzed, and the solid residue was separated, dried and later evaluated for the reuse of salts, insoluble metal hydroxides and later stored and or discarded.

3. Results and Discussion

The results presented in Table 2 show the variations of the parameters analyzed before and after the electrocoagulation, showing the removal of dissolved compounds and the efficiency of the treatment by electrocoagulation/flocculation. The solid residue (treatment sludge) was dried in an oven and subsequently analyzed so that the mass balance of the removed and generated compounds could be checked.

Table 2   Variations in the physical and chemical parameters of the treated residues.

Parameters											
Residue		pH	Conductivity (mS/cm)	Turbidity (NTU)	Alkalinity (mg/L CaCO$_3$)	Chloride (mg/L)	COD (mg/L)	Suspended Solids (mg/L)	Color	Current (A)	Time (hours)
01	A	7.56	2.83	72.2	0.6459	0.9341	693.93	215	Cobalt Blue	4	4
	E	8.52	3.08	2.35	0.43676	0.7144	908.6	22	Slightly bluish	4	4
02	A	7.75	2.70	147	0.7866	0.4161	783.93	171	Cobalt Blue	4	4
	E	9.66	2.54	0.1	0.2647	0.3256	496.93	17	Colorless	4	4
03	A	0.94	2.37	102	ND	0.97	799.93	68	Purple	4	3
	E	9.18	3.52	0.1	0.4932	0.5997	1023.6	18	Colorless	4	3

Residues 1 and 2 presented before the reaction cobalt blue color and parameters suggestive of the presence of weak bases in a dynamic equilibrium, strong base in very diluted solution and hydrolyzable salts, metal complexes Cu (II), Co (II), Cr (II), Pb (I), Ag (I), which generate weak bases and weak acids in aqueous medium. Residue 3 was purple in color with conductivity values between 2.37 mS/cm and pH 0.94 indicating the presence of strong dissociated acids in high concentrations.

After the electrocoagulation process, the pH values of the residues changed significantly. According to Kobya et al. (2006), the variation is attributed to the buffer capacity of the system $Al^{3+}/Al(OH)_3$. For aluminum electrodes in the electrocoagulation-flocculation process, when the initial pH is less than 8, the final pH increases and for higher values the final pH decreases. For each pH range, an aluminum species is released, for example: when the pH is in the range 2-3, Al^{3+} and $Al(OH)_2^+$ species predominate; when the pH is between 4-9, Al^{3+} OH$^-$ions are generated by the electrodes that react to form species such as $Al(OH)_2^+$, $Al(OH)_2^{2+}$, $Al_6(OH)_{15}^{3+}$, $Al_7(OH)_{17}^{4+}$, $Al_{13}(OH)_{34}^{5+}$, which ultimately become $Al(OH)_3$ by means of complex polymerization/precipitation mechanisms. For pH greater than 8 the concentration of the $Al(OH)^{-4}$ anion increases, significantly reducing the concentration of $Al(OH)_3$ [4].

In addition to the above, when the pH of the effluent remains in the range between 7 and 8, the sweeping flocculation mechanism is favored, especially if the solid form of aluminum hydroxide $Al(OH)_3$ predominates in the liquid medium [5], which explains the pH variation in electrocoagulated residues 1, 2 and 3.

Holt et al. (2002) [6] observed that the species of complexes formed in the oxidation of the aluminum electrode vary depending on the pH of the medium. For pH between 3 and 5, species of the type $[Al(OH)_2^+]$ and $[Al(OH)^{3+}]$ predominate, while for pH greater than 6 the species $Al(OH)_3$ predominates, which can generate a gelatinous layer at a pH above 7.0. According to Chen et al. (2000) [7] the increase in pH can occur from other mechanisms such as the transfer of CO_2, because CO_2 is super-saturated in acidic aqueous electrolyte and can be released from the medium due to the agitation caused by the $_2$ bubbles, thus causing the pH to rise.

Before the electrocoagulation-flocculation process, it was observed that in residues 1 and 2 the predominant alkalinity species is bicarbonate ion (HCO_3^-), and it was not detected in residue 3. After the electrocoagulation-flocculation process, bicarbonate and carbonate species were detected in residues 1 and 2 and were not detectable for residue 3. Residue 3 showed 0.6100 mg/L for hydroxyl ions OH$^-$, not observed in the other residues.

According to Alpha (1998) [3], the total alkalinity of a solution is usually due to the hydroxyl, carbonate and bicarbonate ions dissolved in the water and the sum of

the concentrations of these ions is expressed as calcium or sodium carbonate. Furthermore, these same concentrations may vary according to the pH of the environment in which they are found, as the example in Fig. 3, which shows the variation in the concentrations of alkaline species as a function of pH: The relationship between alkalinity and species concentrations is one of the important points, as it allows us to determine which species will contribute to the value of alkalinity and the function of its pH in the residues. Drawing a comparison with the graph in Fig. 3, we observed that theoretically in the pH value range between 7 to 8 the species with the highest concentration is the HCO_3^- ion, and in pH ranges from 11 to 14 the concentrations of the carbonate ion species (CO_3^{-2}), hydroxyl ion (OH^-) are predominant, suggesting that the alkalinity of residues 1, 2 and 3 has a contribution to the concentration of these species. Residue 3 showed concentration only for the OH^- ion, which justifies the pH > 9 value.
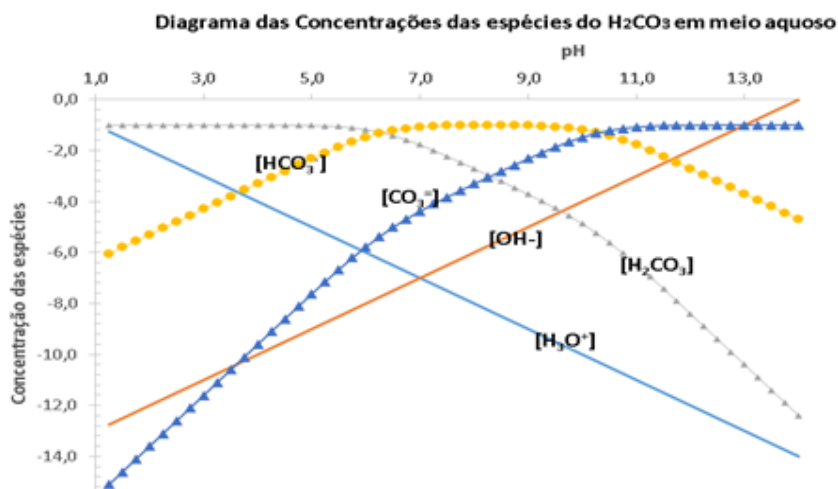

Fig. 3   Diagram of the concentrations of the weak acid species from the hydrolysis of the carbonate ion in the residue.

Residues 1, 2, 3 before electrocoagulation-flocculation showed residual values for chlorides mg/L, 0.9341 mg/L, 0.4161 mg/L and 0.9700 mg/L, respectively, probably from the ionization of hydrochloric acid HCl and the dissociation of chloride salts from alkali, alkaline earth and transition metals. When submitting residues to the electrocoagulation-flocculation process, it is observed that the concentration of the Cl^- chloride ion decreases in all residues: 0.7144 mg/L, 0.3256 mg/L and 0.5997 mg/L, respectively.

The values for electrical conductivity increased for all residues, residue 1 (2.83-3.08 µS/cma), residue 2 (2.20-2.54 µS/cma) and residue 3 (2.37-3.52 µS/cma). The results suggest an increase in molar conductivity as the concentration decreases in chloride and nitrate ions, tending to a maximum value, known as limiting molar conductivity, represented by the symbol Λ∞. In this case, we point out the presence of some electrolytes such as sodium chloride (NaCl), nitrates contributing to the increase in molar conductivity (strong electrolytes).

The effluent subjected to the treatment under agitation promotes an increase in the migration of cations and anions from the solution to the electrolyte, causing an increase in the reaction speed and consequently the oxidation of matter. The greater this agitation, the greater the speed of the reaction. This explains the increase in molar conductivity in the residues and a decrease in the concentration of Cl^- chloride and NO_3^- nitrate ions. The flocculation and precipitation of silver chloride and mercury may also be responsible for decreasing the concentration of the chloride ion in residues 1 and 2.

The residues showed high values for dissolved solids before the coagulation-flocculation process, suggestive of the amount of insoluble salts in them. The values

varied after the electrolytic process: 215 mg/L-22 mg/L for residue 1, 171 mg/L-17 mg/L for residue 2 and 68 mg/L-18 mg/L for residue 3. This shows the efficiency of electrocoagulation and flocculation, making residues look limpid and transparent.

The increase in current intensity causes an increase in the migration of cations from the solution to the cathode with the deposition of anion and an increase in the migration of anions from the solution to the anode with the respective deposition of cations into the solution. Thus, an increase in the reaction rate is generated and serves to characterize the equilibrium kinetics by increasing the current density. The answer to the reaction dynamics is to increase the concentration in mg/L of removal of COD (Chemical Oxygen Demand), observed in the treatment of residue

1 (693.93 mg/L-908.60) and (496.93 mg/L-757.93 mg/L) for residue 2 and (799.93 mg/L-1023.6 mg/L) for residue 3, which gives an increase in efficiency in the treatment process. The process proved to be very efficient in decreasing turbidity, which increased during the electrocoagulation reaction and after the electroflocculation decreased to reduced values. All residues had a decrease in initial turbidity and color, thus suggesting a reduction in dissolved compounds.

3.1 Electrode Wear and Aluminum Release

The plates (sacrifice electrodes), Fig. 4, with a total submerged area of 400 cm² each, were weighed before and after the electrocoagulation/flocculation: Plate 1 (325.25 g-314.10 g), Plate 2 (321.64 g-300,88).

Fig. 4   Aluminum electrode.

Mass loss was calculated according to Eq (1):

$$M_{el} = \frac{i \times t \times M}{n \times F} \qquad (1)$$

Where i is the current in ampere, t is the treatment time in seconds, M is the molar mass of the electrode's predominant element in g/mol, n is the number of electrons involved in anode oxidation and F is the Faraday constant 9.65×10^4 Cmol^{-1}.

In the treatment stage there was a significant loss of electrode mass of 5.37g of aluminum for the medium, however the theoretical value of the amount of Al^{+3} released to be consumed during electrolysis as a coagulant doser, is the important mechanism to form

aluminum hydroxide Al(OH)$_3$. In fact, according to Meneses et al. (2012) [2], since coagulation is achieved by charge neutralization and destabilization of negatively charged colloids by the cationic hydrolysis of Al^{3+} products, excess coagulant can give a reverse charge and stabilization of colloids.

4. Conclusion

Considering the results obtained in the experiments carried out with the electrocoagulation/ electroflocculation system and analyzing the acceptable limits for legal disposal, issued by CONAMA Resolution 403/2011, it can be inferred that

the system is efficient and removes most of the dissolved substances or in suspension of liquid effluents from teaching and research laboratories. The implementation of a residue treatment program involves an awareness of the need to adopt new habits in order to meet not only the current legislation, but mainly a new mentality that is concerned not only with the quality of the analyzes, but also with residue management. This view involves identifying, treating and referring them, in a way that reduces possible impacts on the environment.

Acknowledgements

References

[1]   M. Y. A. Mollah, R. Schennach, J. R. Parga and D. L. Cocke, Electrocoagulation (EC) — Science and applications, *Journal Hazardous Materials* 48 (2001) 29-41.

[2]   J. M. Meneses, R. F. Vasconcelos, T. F. A. Fernandes and T. G. Araujo, *Unidade Acadêmica de Engenharia Química*, Universidade Federal de Campina Grande, Rua Aprígio Veloso, 882, Bloco CM, 58429-140 Campina Grande – PB, Brasil, 2012, pp. 335-340, available online at: http://submission.quimicanova.sbq.org.br/qnol/2012/vol35n2/01-AR10709.pdf.

[3]   Alpha, *Standart Methods for Examination of Water and Wastewater* (20th ed.), American Public Health association, American water work Association, Water Environmental Federation, Washington, 1998.

[4]   B. Merzouk, B. Gourich, K. Madani, C. Vial and A. Sekki, Removal of a disperse red dye from synthetic wastewater by chemical coagulation and continuous electrocoagulation. A comparative study, *Desalination* 272 (2011) 246-253.

[5]   F. N. Crespilho, C. G. Santana and M. O. Rezende, *Quim. Nova* (2004) 27-37.

[6]   P. K. Holt, G. W. Barton, M. Wark, and C. A. Mitchell, A quantitative comparison between chemical dosing and electrocoagulation, *Colloids Surf.* 211 (2002) 233-248.

[7]   X. Chen, C. Chen and P. I. Yue, *Sep Purif. Technol.* (2000) 19-65.