

Removal of organic load and suspended solids from water by electrocoagulation method

¹Ilie PISOI, ²Cristian DANIELESCU, ³Florica MANEA, ⁴Smaranda MASU, ²Cecilia SAVII, and ³Georgeta BURTIČĂ

¹SECOM Company, Drobeta-Turnu Severin, Romania; ²Institute of Chemistry Timisoara of Romanian Academy, Timisoara, Romania; ³"Politehnica" University of Timisoara, Timisoara, Romania; ⁴National Research and Development Institute for Industrial Ecology-ECOIND, Timisoara, Romania. Corresponding author: F. Manea, florica.manea@chim.upt.ro

Abstract. Electrocoagulation (EC) is an electrochemical technique involving in-situ generation of coagulation agents from sacrificial anodes by type of aluminium and iron. In the present study EC has been evaluated as a treatment technology for organic load and suspended solids removal from a real wastewater proceeded from pulp and paper industry, which was characterized by high content of organic load and suspended solids. The efficiency of the electrocoagulation process was assessed by monitoring Chemical Oxygen Demand (COD) and suspended solids (s.s.) parameters. Laboratory- scale experiments were conducted with aluminum anode to assess its efficiency under galvanostatic regime. To establish the optimum operational parameter selected as current density, the electrolysis was carried out at 50, 100 and 200 Am⁻². The electrocoagulation process performance was assessed based on the efficiencies of COD and s.s. removal correlated with the specific electrical energy consumption. Applying EC process allowed to achieve the COD removal efficiencies ranged between 83.80 and 94.00 % and s.s. removal efficiencies between 87.77 and 95.47 %.

Key Words: wastewater, pulp and paper industry, electrocoagulation, aluminium anodes.

Introduction. Pulp and paper industry is severely polluting the environment, especial because of large volumes of wastewater discharged into the aquatic environments. This kind of pulp and paper wastewater, containing mainly toxic organic substances, is characterized by a high level of chemical oxygen demand (COD) and suspended solids (s.s.). Thus, the wastewater treatment to reduce any possible impacts on the aquatic environment is required (Gavrilescu & Puitel 2007; Gavrilescu & Bobu 2009; Patel & Suresh 2008; Wang et al 2006ab). In general, the wastewater treatment is a real challenge for many of the industries to comply with applicable effluent standards, which are established in relation with the receiver environment.

There are several conventional wastewater treatment methods, including physical, chemical and biological methods (Babu et al 2007; Budiyo et al 2010; Carneiro et al 2003; Inan et al 2004; Mouli et al 2004; Raghu & Basha 2007). End-of-pipe treatment of wastewaters can be accomplished by integration of traditional biological treatment processes with physical-chemical applications. The biological methods are very effective for the treatment of wastewater with a high value of biological oxygen demand (BOD), but they are ineffective if recalcitrant organic compounds are present because they must be supported by a physical-chemical treatment. Coagulation is one of the most commonly used techniques. In coagulation operations, a coagulation agent is added to a colloidal suspension to cause its destabilization and flocculation. However, this technology usually needs additional chemicals which produce a huge volume of sludge (Raghu & Basha 2007).

Electrocoagulation technology offers an alternative to conventional coagulation process, based on the electrochemical in-situ generation of the coagulation agents without direct addition of any chemicals (Belkacem et al 2008; Zaharia et al 2005).

Coagulants are produced by the electrolytic oxidation of appropriate anode materials, such as stainless steel and aluminum electrodes, which result in formation of highly charged polymeric metal hydroxyl species. These species neutralize the electrostatic charges on the suspended solids and facilitate agglomeration resulting in separation from the aqueous phase (Ciorba et al 2000; Ciorba et al 2002).

In comparison with the traditional conventional coagulation process, various advantages of electrocoagulation process have been reported (Mollah et al 2001; Rajeshwar & Ibanez 1996). Thus, the electrocoagulation process can be regarded as a green technology in relation with both the clean reagent that is the electron and no adding any chemicals to produce secondary pollution. Another important advantage is given by the simplicity and compactness of the treatment facility and there is a possibility of complete automation. Electrocoagulation process has the advantage of removing the smallest colloidal particles, the flocs formed during the electro coagulation process tends to be much larger, therefore can be separated by filtration. It is a low sludge producing process, and the sludge formed during the process tends to be readily settable and easy to dewater.

In this paper are presented some results regarding the assessment of the electrocoagulation application on a real wastewater proceeded from pulp and paper industry. The optimum operating conditions under galvanostatic regime were established based on the current density, electrolysis time and the specific electrical energy consumption. The electrocoagulation performance assessed in relation with chemical oxygen demand (COD) and suspended solids (s.s.) removal was compared with simple conventional coagulation using the optimum dose of aluminium sulphate.

Material and Method. A real raw wastewater proceeded from a pulp and paper factory was used for the laboratory experiments. The quality of the raw and treated wastewaters was monitored in terms of COD (for organic load) and s.s.(suspended solids) parameters. The quantitative determinations of COD and s.s. parameters were made in according with American Standard Methods (Franson 1995).

The removal of pollutants by electroflotocoagulation and separation was carried out in the electrolysis cell at galvanostatic condition. The schematic presentation of the experimental set-up was presented in our previous study (Bebeseselea et al 2006). The characteristics of raw wastewater are gathered in Table 1. The electroflotocoagulation process was operated at different current densities to determine the optimum operating variables in terms of current density and the electrolysis time. The assessment of the electrocoagulation process was based on both the removal process efficiency and the energy consumption.

Table 1

The characteristics of raw wastewater proceeded from pulp and paper industry

Parameter	pH	COD (mgO ₂ L ⁻¹)	s.s. (mgL ⁻¹)	Cl ⁻ (mgL ⁻¹)	SO ₄ ²⁻ (mgL ⁻¹)
Value	6.73	2285	3600	350	525

The removal process efficiency in relation with suspended solids and chemical oxygen demand after electrocoagulation treatment was determined based on the equation (1):

$$\text{Removal efficiency (\%)} = [(C_0 - C)/C_0] \times 100 \quad (1)$$

The specific energy consumption, W_{sp} , was calculated with the relation (2):

$$W_{sp} = \frac{(Q \cdot V^{-1})U}{1000} \quad (\text{kWh dm}^{-3}) \quad (2)$$

Al₂(SO₄)₃*18H₂O reagent provided by Chimopar Bucuresti was used for the coagulation experiments. Coagulation experiments were carried out using Degremont Jar Test method in batches of 1L. After the addition of the coagulants, the samples were subjected to rapid mixing for two minutes at 250 rpm, then for 10 minutes at 25 rpm and last settling for 30 minutes, without pH correction. The supernatant was analyzed. Optimal dose for coagulant agent was determined also according to COD and s.s.

Results and Discussion. Taking into account the characteristics of raw water in relation with the presence of chloride and sulphate, the electrolysis experiments were carried out without any adding of supplementary salts, which are usually necessary for electrochemical treatment. Based on our previous study (Bebeselea et al 2006) the experiments were conducted at three current densities, *i.e.*, 50, 100 and respective, 200 Am⁻².

Table 2 presents working condition and the assessment of process control parameters, *i.e.*, COD and s.s. removal efficiency and specific electrical energy consumption. The used quantity of electricity (charge consumed) is expressed as Ah/dm³ for batches of 500 cm³.

Table 2

Evolution of the electroflotocoagulation process
under current density of 50 A/m²

Q/V (Ah/dm ³)	time (minutes)	U (V)	W _{sp} (kWh/m ³)	pH _f	COD (mgO ₂ L ⁻¹)	s.s. (mgL ⁻¹)
0.1	15	8.7	0.87	7.74	177.0	440
0.4	60	11.7	4.68	7.77	151.0	240
0.8	120	14.6	11.68	7.90	146.0	230
1.0	150	15.0	15.00	8.11	142.0	220
1.2	180	15.3	18.36	8.18	137.0	163

The main electrochemical reactions that occur during the electrolysis at galvanostatic conditions can be described by active dissolution of anode (aluminium), cathodic hydrogen evolution, leading to the pH increasing and aluminium hydroxicomplexes species formation. Increasing local pH favoured the generation of the aluminium hydroxicomplexes, which can be adsorbed on the colloids and creates bridges between the particles. In addition, the amorphous solid aluminium hydroxide flocs that forms at elevated pH, settle down causing sweep flocculation. The electrocoagulation process involves three successive stages (Mollah et al 2001), *e.g.*, formation of coagulants by electrolytic oxidation of the sacrificial anode electrodes, destabilization of the contaminants, particulate suspension, and the aggregation of the destabilized phases to form flocs.

The main reactions that occur during the electrolysis under galvanostatic conditions can be described by active dissolution of anode (aluminium), cathodic hydrogen evolution, a pH increase and aluminium hydroxicomplexes species formation, as follows:

Al anode reactions:



Stainless steel cathode reactions:



Bulk solution:



pH affected the electrocoagulation mechanism, especial in bulk solution. At low pH values of 2–3, cationic monomeric species Al³⁺ and Al(OH)₂⁺ predominate. When pH is between 4–9, the Al³⁺ and OH⁻ ions generated by the electrodes react to form various monomeric species such as Al(OH)²⁺, Al(OH)₂²⁺, and polymeric species by type of

$\text{Al}_6(\text{OH})_{15}^{3+}$, $\text{Al}_7(\text{OH})_{17}^{4+}$ and $\text{Al}_{13}(\text{OH})_{34}^{5+}$ that finally transform into insoluble amorphous $\text{Al}(\text{OH})_3(\text{s})$ through complex polymerization/precipitation kinetics [26]. When pH is higher than 10, the monomeric $\text{Al}(\text{OH})_4^-$ anion concentration increases to $\text{Al}(\text{OH})_3(\text{s})$ detriment.

Two main mechanisms are generally considered for electrocoagulation in the bulk solution: precipitation for pH lower than 4 and adsorption for higher pH. Adsorption may proceed on $\text{Al}(\text{OH})_3$ or on the monomeric $\text{Al}(\text{OH})_4^-$ anion depending on the pollutant chemical structure. The formation of $\text{Al}(\text{OH})_3(\text{s})$ is optimal in the 4–9 pH range, and this pH was used in this work.

The main electrode processes can be partially activated or inhibited on the presence of organic and suspended matter by adsorption on electrode and involvement in surface film formation. Also, the presence of Cl^- , SO_4^{2-} anions influences the aluminium dissolution, with further involvement in the electrocoagulation process.

The theoretical doses of electrochemical dissolved aluminium were calculated based on the Faraday's law presented in equation (9):

$$w = itM/ZF \quad (9)$$

where: w = aluminium dissolving (g),

i = current (A),

t = time (s),

M = molecular weight of Al

Z = number of electrons involved in the redox reactions and

F = Faraday's constant = 96500 C/mol

Also, the experimental dissolved aluminium doses were determined by electrode weighing before and after electrolysis. Under studied conditions, the over-Faradays dissolution behaviour of aluminium anode was achieved, which represents the common aspect for aluminium. This informs that no inhibition of the aluminium dissolution occurred under the conditions of $350 \text{ mgL}^{-1} \text{ Cl}^-$ and $525 \text{ mgL}^{-1} \text{ SO}_4^{2-}$.

Figures 1 and 2 present the technical results of the electrocoagulation application on the real wastewater proceeded from pulp and paper industry at the three current densities. Under all current densities, the quality of the treated wastewater is suitable for discharging into the sewerage and not into the natural receiver. However, the very good efficiencies higher than 90 % were reached for the current density of 50 Am^{-2} . For comparison, the classical coagulation using aluminium sulphate was studied by Jar-test method and the optimum dose of aluminium sulphate was $22.5 \text{ mg Al L}^{-1}$ (the results are not shown here). For this optimum dose, the coagulation efficiency was worse than the electrocoagulation one.

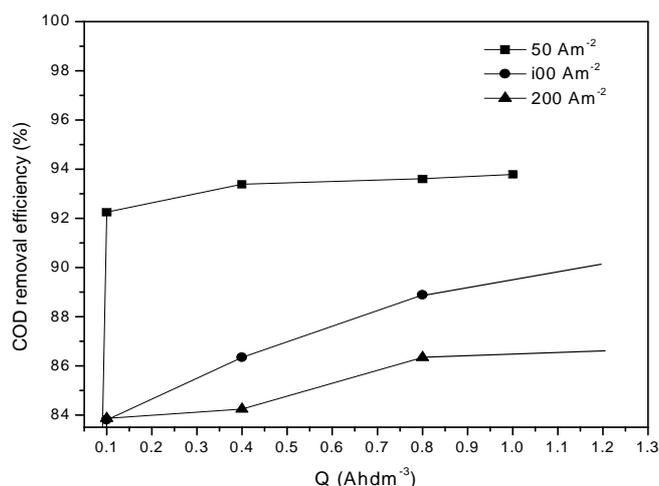


Figure 1. Evolution of COD removal efficiency versus charge consumed during electrocoagulation process at different current densities.

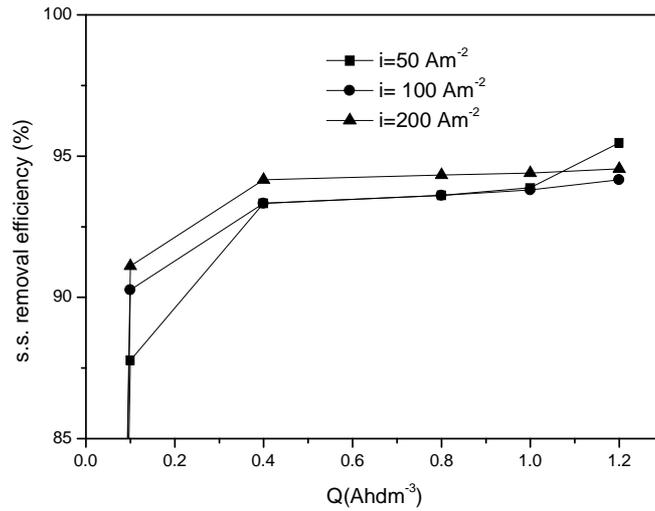


Figure 2. Evolution of s.s. removal efficiency versus charge consumed during electrocoagulation process at different current densities.

A major aspect regarding the assessment of the electrochemical performance is the specific electrical energy consumption, which has to be correlated with the best treatment performance. The results related to electrical energy consumption for electrocoagulation process are showed in Figure 3. As we expected, the lowest specific electrical energy consumption was reached under the conditions of the current density of 50 Am⁻². To determine the duration of the electrocoagulation application, the dependence of the electrolysis time at each current density versus the charge consumed during the electrolysis is shown in Figure 4. Based on the technical-economical point of view, the assessment of the electrocoagulation process on the wastewater with the specific characteristics, the operating conditions was established as the current density of 50Am⁻² for the electrolysis time of 60 minutes with the specific electrical energy consumption of 4 kWhm⁻³.

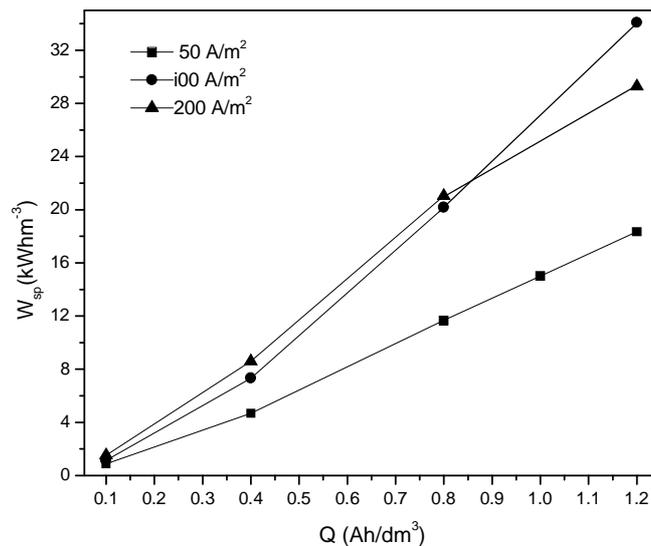


Figure 3. Evolution of specific electrical energy consumption versus charge consumed during electrocoagulation process at different current densities.

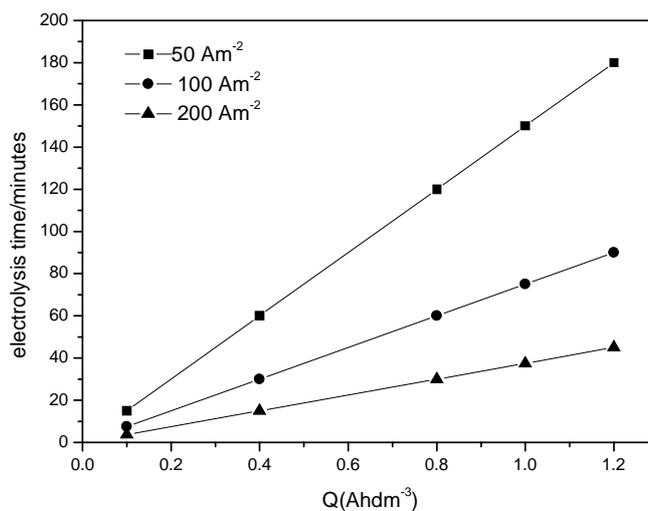


Figure 4. Dependence of the electrolysis time versus charge consumed during electrocoagulation process at different current densities.

Conclusions. The application of electrocoagulation process in the removal of organic load and suspended solids from a real wastewater proceeded from pulp and paper industry given good results, the removal efficiency of COD reached 94 % and the removal efficiency of suspended solids reached 95.5 % for the current density of 50 Am⁻² after 180 minutes of the electrolysis time. The electrocoagulation results were better versus simple coagulation using aluminium sulphate at optimum dose. The real wastewater composition allowed the application of electrocoagulation process without a supplementary adding of supporting electrolyte (chloride and sulphate). The optimum working conditions should be selected based on a certain removal efficiency taking into account the dependence between the specific electrical energy consumption, the current density and the electrolysis time.

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Authors:

Ilie PISOI, SECOM Company, street Carol I, no. 53, Drobeta-Turnu Severin, Romania.

Cristian DANIELESCU, Institute of Chemistry Timisoara of Romanian Academy, 24 Mihai Viteazu Ave., 30022, Timisoara, Romania.

Florica MANEA, "Politehnica" University of Timisoara, P-ta Victoriei, no. 2, 300006, Timisoara, Romania; e-mail: florica.manea@chim.upt.ro

Smaranda MASU, National Research and Development Institute for Industrial Ecology-ECOIND, Timisoara, Romania.

Cecilia SAVII, Institute of Chemistry Timisoara of Romanian Academy, 24 Mihai Viteazu Ave., 30022, Timisoara, Romania.

Georgeta BURDICĂ, "Politehnica" University of Timisoara, P-ta Victoriei, no. 2, 300006, Timisoara, Romania.

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