

Electrocoagulation: A Novel Waste Water Treatment Method

Satish.I. Chaturvedi

Department of Chemical Engineering, SVM Institute of Technology, Bharuch, Gujarat, India

ABSTRACT: A renewed interest in electrocoagulation has spurred by the search for reliable, cost effective method for the treatment of polluted water. Electrocoagulation present a robust novel and innovative alternative in which a sacrificial metal anode corrodes, due to an applied electric potential, while the simultaneous evolution of hydrogen at the cathode which is removed by flotation. This has the major advantage of providing active cations required for coagulation, without increasing the salinity of the water. Electrocoagulation is a complex process with a multitude of mechanisms operating synergistically to remove the pollutants from the water. Different options exist for key mechanisms and reactor configurations. This paper presents an in-depth discussion and consideration of the factors that are the requirements for the optimum performance of this technology.

Keywords: Chemical process, electrocoagulation, metal removal, physical process, wastewater

I. Introduction

The major challenges for the 21st century are water and energy. Due to increased pollution from point and non-point sources quality of the water become a crucial problem, particular for the Third-World Countries. The promising methods based on electrochemical technology are electrocoagulation, electro flotation [1], electro decantation, and others [1-3].

Electrocoagulation (EC) consists of number of benefits [3]: compatibility, amenability to automation, cost effectiveness, energy efficiency, safety, and versatility. Though EC has received little scientific attention a decade back, in the last couple of years, this technology has been widely used for the treatment of dilute wastewaters having heavy metals [4], foodstuff [5-7], oil wastes [8,9], textile and dyes [10-15], fluorine [16], polymeric wastes [17], organic matter from landfill leachate [18], suspended particles [19-22], chemical and mechanical polishing wastes [23], aqueous suspension of ultrafine particles [24], nitrate [25], phenolic waste [26], arsenic [27], and refractory organic pollutants including lignin and EDTA [28]. Also, electrocoagulation is applicable for drinking water treatment [29, 30]. This process has capability to overcome the disadvantages of the other treatment techniques.

II. Theory of Electrocoagulation

The electrocoagulation process operates on the base of the principle that the cations produced electrolytically from iron and/or aluminum anodes shown in fig (1) which is responsible for the increasing of the coagulation of contaminants from an aqueous medium. Electrophoretic motion tends to concentrate negatively charged particles in the region of the anode and positively charged particles in the region of the cathode. The consumable metal anodes are used to continuously produce polyvalent metal cations in the region of the anode. These cations neutralize the negative charge of the particles moved towards the anodes by production of polyvalent cations from the oxidation of the sacrificial anodes (Fe and Al) and the electrolysis gases like Hydrogen evolved at the anode and oxygen evolved at the cathode. Electrocoagulation is an enigmatic technology. One possible conceptual framework is shown in following fig (3) each foundation area brings to ascertain perspective to electrocoagulation, as represented by each lobe of this Venn diagram. The main aim is to shoe how electrocoagulation's complexity can be simplified by using reductionist approach. Relevant phenomena, characterization methods and tools are mentioning each lobe. Above fig. represents the two removal paths with the relative importance of each being set by a combination of reactor design and operating parameters. Current density represented by a doubled-headed arrow at the base between the flotation and coagulation lobes as it determines both the coagulant dosage and bubble production rates as well as influencing the extent of mixing within a reactor. This process involves three successive stages:

- (i) Formation of coagulants by electrolytic oxidation of the 'sacrificial electrode'
- (ii) Destabilization of the contaminants, particulate suspension and breaking of emulsions
- (iii) Aggregation of the destabilized phase to form flocks.

Destabilization mechanism of contaminants, particulate suspension, and emulsion breaking summarized as follows:

- (i) Due to oxidation of the sacrificial anode, generation and interaction of ions are possible. Compression of the diffuse double layer can be possible around the charged ions.
- (ii) Electrochemical dissolution of the sacrificial anode produced counter ions. These counter ions are responsible for presence of charged neutralization of ionic species which present in the waste water. These counter ions are responsible of the reduction of the electrostatic interparticle repulsion so that van der Waals attraction predominates hence coagulation occurs which approach to the zero net charge.
- (iii) Coagulation causes a flock formation and creates a sludge blanket which entraps and bridge colloidal particles which is present in the still aqueous medium.
- (iv) The negative surfaces of the solid oxides, hydroxides, and oxyhydroxides are responsible for adsorption of contaminated contents.

(v) Due to dissolution of Fe or Al electrodes from the anode respective metal ions are generated. These ions are immediately hydrolyzed into polymeric ions or aluminum hydroxide.

Main function of sacrificial anode is to generating polymeric hydroxides nearby the anode. These polymeric hydroxides are act as a excellent coagulating agents. Due to electrophoretic action negative ions which are produce from the cathode moves towards the anode. Due to combination of the metal cations with these negative particles which turns into the coagulation. Due to electrolysis is continuously carried out, water is electrolyzed. At anode small bubble of oxygen and at the cathode small bubbles of hydrogen are generated which are responsible of electrolysis of water. The flocculated particles attract by these bubbles and these flocculated particles float due to the natural buoyancy towards the surface Physiochemical reaction also occurs in the electrocoagulation cell as follows [31].

- (i) At the cathode metal ions reduction take place.
- (ii) In the waste water impurities are responsible for cathodic reduction.
- (iii) Colloidal particles being generated by electrode erosion.
- (iii) Coagulation and discharge of colloidal particles by electroflotation or sedimentation and filtration.
- (iv) Ions migration done due to electrophoretic in the solution.
- (v) Oxygen and hydrogen bubbles which are produced at anode and cathode,
- (vi) Responsible of electroflotation of coagulated particles.
- (vii) Other chemical and electrochemical process occurs.
- (viii) Electrocoagulation process carried out by an external power supply.

The quantity of electricity passed through is actually responsible for dissolution and deposition of metal ions at the electrodes. A relationship between current density (A/cm^2) and the quantity of the metals (M) dissolved (g of M/cm^2) find out by using Faraday's law:

$$W = i \times t \times M / n \times F, (1)$$

W = the amount of dissolution of electrode (g of M/cm^2)

i = Current density (A/cm^2)

t = time in second

M = Relative molar mass of the electrode

n = no. of electrons in oxidation/reduction reaction

F = Faraday's constant, 96,500 C/mol.

Electrocoagulation operating conditions are mostly dependent on the chemistry of the aqueous medium, mainly conductivity and pH. Also other important characteristics are particle size, type of electrodes, retention time between plate, plate spacing and chemical constituent concentrations. The mainly operating principal is that the cations produced electrolytic from iron and/ or aluminum anodes enhance the coagulation of contaminants from an aqueous medium.

Electrophoretic motion tends to concentrate positively charged ions in the regions of the cathode and negatively charged particles in the region of the anode. The sacrificial metal, anode are used to continuously produced polyvalent metal cations in the in the vicinity of the anode. These cations neutralize the negative charge of the particles carried to the anode by electrophoretic motion, which facilitating coagulation.

Generally, oxidation of organic matter by electrochemical treatment can be classified as direct oxidation at the surface of anode and indirect oxidation from the anode surface which are influenced by the anode material. Oxidation of organic matter depend upon the anode material, concentration of NaCl and current and voltage applied. In addition, electrocoagulation also occurs during electrochemical treatment of waste water. The electrocoagulation mechanism has been proposed for the production of $Fe(OH)_3$ or $Fe(OH)_2$.

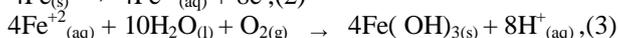
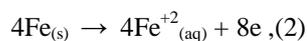
III. Reaction Mechanism

Electrocoagulation is a complex process occurring via series steps. When current is passed through electrochemical reactor, it must overcome the equilibrium potential difference, anode over potential, cathode over potential and potential drop of the solution. The anode over potential includes the activation over potential and concentration potential, as well as the possible passive over potential resulted from the passive film at the anode surface, while the cathode over potential is principally composed of the activation over potential and concentration over potential. Reactions at electrode surfaces, formation of coagulants in aqueous phase, adsorption of soluble or colloidal pollutants on coagulants shown in fig. (2).

Generally, aluminum and iron are used as an electrode material in the electrocoagulation process. In the iron electrode, two mechanisms have been proposed [32-39].

Mechanism 1:

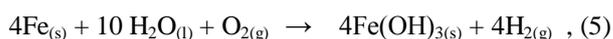
Anode:



Cathode:

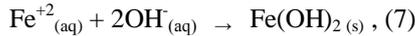
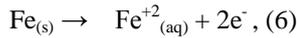


Overall:



Mechanism 2:

Anode:



Cathode:



Overall:

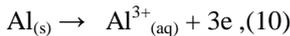


Due to oxidation in an electrolyte system, iron produces form of monomeric ions, $\text{Fe}(\text{OH})_3$ and polymeric hydroxy complex such as:

$\text{Fe}(\text{H}_2\text{O})_6^{3+}$, $\text{Fe}(\text{H}_2\text{O})_5^{2+}$, $\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2^{+}$, $\text{Fe}(\text{H}_2\text{O})_8(\text{OH})_2^{4+}$ and $\text{Fe}_2(\text{H}_2\text{O})_6(\text{OH})_4^{4+}$ depending upon the pH of the aqueous medium.

In the case of Aluminum electrode, reactions are as follows:

Anode:



Cathode:



For the aluminum electrodes, $\text{Al}^{3+}_{(aq)}$ ions will immediately undergo further spontaneous reaction to generate corresponding hydroxides and polyhydroxides. Due to hydrolysis of Al^{3+} , $\text{Al}(\text{H}_2\text{O})_6^{3+}$, $\text{Al}(\text{H}_2\text{O})_5\text{OH}_2^{+}$, $\text{Al}(\text{H}_2\text{O})(\text{OH})_2^{2+}$ generated. This hydrolysis products produced many monomeric and polymeric substance such as, $\text{Al}(\text{OH})^{2+}$, $\text{Al}(\text{OH})_2^{+}$, $\text{Al}_2(\text{OH})_2^{4+}$, $\text{Al}(\text{OH})_4^{+}$, $\text{Al}_6(\text{OH})_{15}^{3+}$, $\text{Al}_7(\text{OH})_{17}^{4+}$, $\text{Al}_8(\text{OH})_{20}^{4+}$, $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$, $\text{Al}_{13}(\text{OH})_{34}^{5+}$ [38].

Within the electrocoagulation reactor, several distinct electrochemical reactions are produced independently. These reactions are as follows:

- (i) Seeding: This is resulting from the anode reduction of metal anions that becomes very centers for larger, stable, insoluble complexes that precipitate as complex metal ions.
- (ii) Emulsion breaking: Due to the oxygen and hydrogen ions that bond into the water receptor sites of oil molecules creating a water in soluble complex separating water from oil, mud, dyes inks, etc.
- (iii) Halogen complexing: As the metal ions bind into a chlorinated hydrocarbon molecules resulting in a large insoluble complexes separating water from pesticides, herbicides, chlorinated PCB's, etc.
- (iv) Bleaching: As the oxygen ions produced in the reaction chamber oxidizes dyes, cyanides, bacteria, viruses, biohazards. Electron flooding of the water eliminates the polar effect of the water complex, allowing colloidal materials to precipitates and increase of electrons creates an osmotic pressure that raptures bacteria, cysts and viruses.
- (v) Oxidation reduction: These reactions are forced to their natural end point within the reaction tank which seeds up the natural process of nature that occurs in wet chemistry.
- (vi) Electrocoagulation induced pH: This is swings toward the neutral.

IV. Comparison of Different Processes

Electrocoagulation is most efficient method with less effected disadvantages. Data in Table no. (1) [43 -56] Indicated the efficiency of electrocoagulation compare to other process.

V. Advantages

- (i) EC requires simple equipment and is easy to operate.
- (ii) EC requires low initial investment with low operating cost.
- (iii) The electrolytic processes in the EC cell are controlled electrically and with no moving thus requiring less maintenance.
- (iv) EC does not require any chemicals. So there is no problem of neutralizing excess chemicals and no possibility of secondary pollution caused by chemical substances..
- (v) EC composed of mainly metallic oxides/hydroxides. Sludge formed by EC tends to be readily settable and easy to de-water, so low sludge generation can be done.
- (vi) EC flock tends to be much larger, contains less bound water, is acid-resistant and more stable, and therefore, can be separated faster by filtration.
- (vii) EC produces effluent with less total dissolved solids (TDS) content as compared with chemical treatments. If this water is reused, the low TDS level contributes to a lower water recovery cost.
- (viii) The EC process has the advantage of removing the smallest colloidal particles, because the applied electric field sets them in faster motion, thereby facilitating the coagulation.
- (ix) The gas bubbles produced during electrolysis can carry the pollutant to the top of the solution where it can be more easily concentrated, collected and removed.
- (x) After treatment EC gives palatable, clear, colorless odorless water with zero discharge.
- (xi) EC handles large variation in the waste streams with multiple contaminants.

(xii) The EC technique can be easily used in rural areas where electricity is not available, since a solar panel attached which may be sufficient to carry out the process.

VI. Disadvantages

- 1) In some EC systems, an impermeable formation of oxides film form on the cathode, so efficiency of electrocoagulation cell.
- 2) High conductivity of the waste water suspension is required.
- 3) Gelatinous hydroxide may tend to solubilised in some cases.
- 4) Due to oxidation, sacrificial anode dissolved in the waste water, so need to be regularly replaced.
- 5) The use of electricity may be expensive in some cases.

VII. Recent Improvements

The EC phenomenon has been known as an electrochemical technique for the last century. It has been used with varying degrees of success for treatment of water and wastewater obtained from various sources. In the treatment of wastewater by a hybrid electrocoagulation–flotation technique [41] by Al electrodes, different EC reactors to evaluate their water treatment performance and found out the best configurations to maximize the treatment efficiency. The EC reactors were configured with water up-flow or cross-flow arrangements. The bipolar electrodes were connected in series via the water, and the monopolar electrodes connected in parallel via copper connectors. The current efficiency (Φ) required for the production of dissolved Al^{3+} due to the passage of electrical charge Q (C) in a volume V (m^3) of water was calculated using Faraday's law:

$$\Phi = 3 \times F \times V / Q, (11)$$

Where F is the Faraday constant.

The specific electrical energy consumption (SEEC) was calculated as a function of the applied cell voltage (U):

$$SEEC[kWh (kg Al^{3+})^{-1}] = nFU/3.6 \times 10^3 M_{Al} \Phi, (12)$$

Where n is the number of moles of electrons per mole of the aluminum dissolved.

It was concluded that an up-flow configuration of the electro coagulator performed better than a horizontal flow configuration, with both bipolar and monopolar electrodes. Also, the performance of the EC process was found to be superior to that of conventional chemical coagulation with aluminum sulphate. As per [40], low frequency (25–75 Hz) sonic field at current densities of 0.1–0.4 $A m^{-2}$ to improve the performance of the EC cell with carbon steel electrodes. During this increase the quantity of iron hydroxides, and thereby enhance coagulation. It was assumed that the applied sonic field enhanced the rates of mass transport. Decreased the thickness of the diffuse double layer at the electrode surface. Activated the electrode surface by generating defects at the crystal lattices of the electrodes. Activated the ions in the reaction zone at the electrodes by ultra-sound waves. Increased the temperature at the electrode surface due to friction between the liquid and the surfaces.

However, disadvantages take place after applying the sonic field. Among other things the acoustic waves may destroy part of the colloidal iron hydroxides as well as the adsorption layer at the surface of the colloidal particles. One of the most important considerations in lowering the cost of the EC process is to minimize the IR-drop to enhance current efficiency. Evolution of oxygen at the anode represents an unwanted leakage of current, which reduces the overall current efficiency. This problem can be minimized through the choice of an anodic material that presents a high over potential for the oxygen evolution reaction near the anode. This high over potential permits the realization of anodic reactions, which are not possible with other materials and in particular, the oxidation of organic compounds with a very high current efficiency.

To achieve this goal, a number different configuration have used binary [41,42] & ternary alloys as well as carbon electrodes and titanium sheets coated with certain active oxides as anodes for electrochemical treatment of wastewater, in particular those containing organic dyes, phenols, chloro-substituted phenols, and tannery wastes. As per configuration of [48] the electrocoagulation of aqueous suspensions of ultrafine kaolin particles in a single stirred cell apparatus and in a continuously flowing system consisting of three cells in series. The coagulation rate was described by a second-order rate equation:

$$dc/dt = -k_1 c^2 (1 - e^{-k_2 t})^2, (13)$$

Where c is the concentration at time t ,

u the electrophoretic velocity of the particles,

$k_2 = u/x$ (x being the geometric parameter of the electrode size),

$k_1 = 4kT/3\mu$ (k is the Boltzmann's constant),

μ = the viscosity of the continuous medium.

This second-order rate equation incorporates the electrophoretic migration of particles, and subsequent release of discharged particles into the bulk. The constant terms in this equation were derived from the basic electrophoretic and coagulation phenomenon, which is dependent on the zeta potential of the suspended particles, the applied voltage, the initial concentration of the particles and the electrode geometry.

In the number of EC experiments with ultrafine kaolin particles in a single stirred cell with electrodes in parallel connections found reasonably similarity with the theoretically in a theoretical model involving the electrolysis voltage required in an EC process, the current density, conductivity of the water/wastewater, the interelectrode distance, and the surface of the electrodes. Experiments were carried out with aluminum electrodes to verify and confirm the theoretical model

and determine the constant terms used in the model. Two mathematical models, one applicable to non-passivated aluminum electrode and the other to passivated aluminum electrodes were proposed and experimentally verified.

The theoretical model is based on the fact that when current passes through the electrochemical reactor, it must overcome the equilibrium potential difference, anode over potential, cathode over potential and IR-drop of the solution. The electrolysis voltage U_0 (V) between electrodes may, therefore, be considered to consist of the following terms:

$$U_0 = E_{eq} + \eta_{a,a} + \eta_{a,c} + \eta_{a,p} + |\eta_{c,a}| + |\eta_{c,c}| + dkj, \quad (14)$$

where

E_{eq} = the equilibrium potential difference between the electrodes,

$\eta_{a,a}$ = the activation over potential at the anode,

$\eta_{a,c}$ = the concentration over potential at the anode,

$\eta_{a,p}$ = passive over potential at the anode,

$\eta_{a,a}$ = activation over potential,

$|\eta_{c,a}|$ = activation over potential at the cathode,

$|\eta_{c,c}|$ = concentration over potential at the cathode,

j = current density (A/m^2),

d = net distance between the electrodes (m),

κ = conductivity of the wastewater,

The oxidation at the anode, reduction at the cathode and hydrolysis reaction in the medium to be considered to evaluate different potential terms by using Tafel equation and Nernst-Planck equation and finally propose the following mathematical relationships for calculations of U_0 values:

$$U_0 = A + \eta_{a,p} + dkj + K_1 \ln j, \quad (15)$$

Where

U_0 = potential,

A and K_1 = constant terms,

J = current density (Am^{-2}),

D = net distance between the electrodes (m),

$\eta_{a,p}$ = anode passive potential (V)

κ = conductivity of the wastewater for a non-passivated electrode, the passive over potential can be neglected. For a passivated electrode the relationship can be rearranged to

$$U_0 = A + dkj + K_1 \ln j + K_2 j n \kappa m, \quad (16)$$

Where

K_2 = constant term.

A , K_1 , K_2 , m and n need to be experimentally determined.

Hybrid process:

Sometimes it becomes necessary to use two or more methods of treatment, i.e. hybrid processes, to ensure efficient treatment of wastewater. The EC technology can be designed into water treatment systems to include membrane separation, reverse osmosis, electro filtration, sludge dewatering, thermo-oxidation and other conventional technologies to enhance the recovery of fine particles and metal ions from wastewater. Removal of coloring materials from dyestuffs using EC with electroflotation has been done by have reported the uses of EC with dissolved air flotation (DAF) for treatments of urban wastewater. Continuous treatment of textile wastewater by combining electrochemical oxidation, coagulation and activated sludge has been mentioned by [58]. EC also been used in conjunction with filtration to remove silica and suspended solids that tend to foul reverse osmosis membranes [57,58].

VIII. Conclusion

Without doubt the provision of an adequate water supply suitable for a diversity of uses by world's growing population is one of the 21st century more pressing challenges. Even in the developed countries, the use of large scale, continuous throughput waste treatment plant is not complete solution. Electrocoagulation has successfully treated a wide range of polluted waste water. But the full potential of EC techniques as a waste water treatment is not yet to be fully realized due to following deficiencies in a number of following key areas:

- It is still an empirically optimized process that requires more fundamental knowledge for engineering design.
- No dominant reactor design exists, adequate scale-up parameters have not been defined, material of construction are varied.
- No widely applicable mechanistically based approach to the mathematical modeling of electrocoagulation reactors.
- Failure to fully appreciate that the performance of an electrocoagulation reactor is largely determined by the interaction that occur between the three foundation technologies of electrochemistry, coagulation and flotation.
- No generic solution to the problem of electrode passivation.

After all electrocoagulation has been used successfully to treat a wide range of polluted wastewaters. But the full potential of EC technique as a wastewater treatment is yet to be fully realized. It is still an empirically optimized process that requires more fundamental knowledge for engineering design. No dominant reactor design exists, adequate scale-up parameters have not been defined, and materials of construction are varied. This technology has excellent future because of numerous advantages and the nature of the changing strategic water needs in the world.

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Figures and Tables

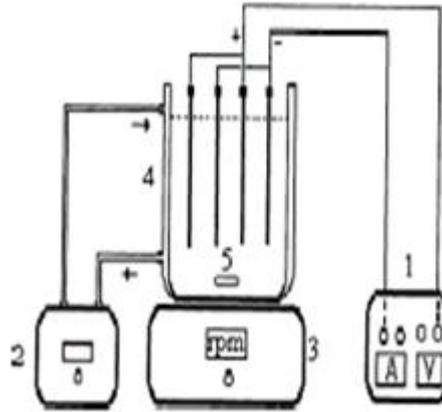
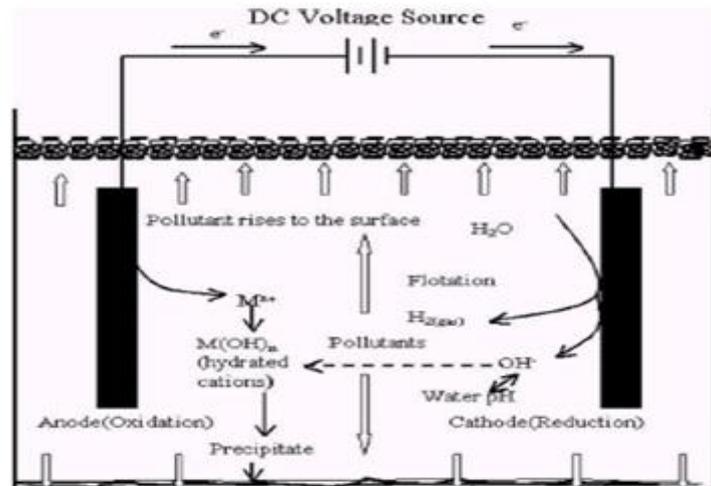
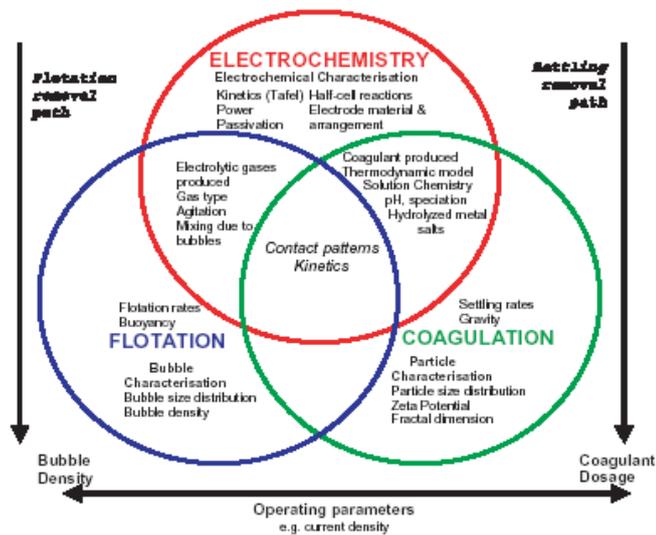


Fig. (1) Schematic diagram of experimental set-up”

1. Digital D.C Power Supply
2. Water circulator
3. Digital Magnetic Stirrer
4. Electrochemical Cell
5. Magnetic Bar Stirrer



“Fig.(2) Schematic diagram of bench-scale two-electrode electrocoagulation cell”



“Fig. (3) Conceptual framework for electrocoagulation as synthetic technology”

TABLE (1) Comparison data of different process

<i>Parameters</i>	<i>Chem. Coag.</i>	<i>Bio logical</i>	<i>Physico-chemical</i>	<i>Membrane & Ion exchange</i>	<i>Electro coagulation</i>	<i>References</i>
Color	89	100	77-100 Coag+Phent o oxidation	99.8 Membrane	100	43 - 47
COD	94	90 - 96	80-100 Coag+Phent o oxidation	99.9 Membrane	87.3 - 87.7	44 - 47
Pb	>99.8	95	> 80 Coag+Phent o oxidation	95 Ion exchange	98.8 ± 1.3	48 - 51
Cu	>99.8	95	>80 Coag+Phent o Oxidation	98 – 99 Ion exchange	> 99.9	48 - 52
Zn	>99.8	95	>80 Coag+Phent o oxidation	98 – 99 Ion exchange	> 99.9	48 - 52
Cr	>99.8	95	>80 Coag+pento oxidation	98 – 99 Membrane & Ion exchange	> 99.8	48 – 50,53
Ni	>99.8	95	>80 Coag+Phent o oxidation	99.8 Membrane	>99.8	48 - 51
Cd	>99.8	95	>80 Coag+Phent o Oxidation	99.9 Membrane	100	48 - 51
As	99	95	>80 Coag+Phent o Oxidation	90 Adsorption	>99.6	49,50,54, 55,56