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Overview of Electrolytic treatment: An alternative technology for purification of wastewater

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ABSTRACT

The rapidly growing world population with increasing level of pollution and continuous need for energy and food is forcing the exploration of the wastewater recycling and resource recovery. Due to the fact that water is a limited and vital resource, it should not be wasted after having been used in industrial processes. One of the main tasks among the emerging technologies is to get high quality water in sufficient quantity at an affordable price from the unused ravage water. In the present scenario, the biological treatments are not sufficient for the reason that they have some disadvantages, such as they take a long time for treatment, require extensive land area for treatment, and the problem of how to get rid of sludge produced by the treatments, whereas the electrochemical remediation methods can be used as an alternative technology for the purification of wastewater contaminated with toxicants. Electrolytic wastewater treatment is rarely used in comparison to chemical treatment. However, this treatment is convenient and may be more efficient to produce high quality water. Electrodes with Aluminum (Al), Iron (Fe), Steel (St) and graphite are generally the best suited to electrochemical water treatment. In the present review, the applications of electrochemical treatment as well as electro-coagulation (EC), electro-flotation (EF) and electro-coagulation/flotation (ECF) to the treatment of wastewater and their operating parameters (reactor design, current density, time and electrode type and arrangement) affecting these processes have been discussed. Among the electrochemical processes, EC process should be the best choice, not only because it can achieve more satisfactory removal but also due to the fact that the process is cost-effective and simple in technological aspect. The major research efforts in the future could be focused on physico-chemical and/or biological treated wastewater for the optimization of electrolytic technology in order to meet the requirement of the desirable/permissible limits of discharged wastewater for its reuse.

Keywords: Wastewater, Electrolysis, Electro-coagulation, Electro-flotation, Current density and Electrode material.

Nomenclature

Al	Aluminum	$FeCl_3$	Ferric chloride
Fe	Iron	ZPO	Zinc phosphate
St	Steel	V	Voltage
C	Carbon	kWh/m^3	Energy consumption
Ti	Titanium	OC	operating cost
DSA	Dimensionally stable anode	US$	US Dollor
EC	Electro-coagulation	I	Current (A)
EF	Electro-flotation	MW	Molecular mass (g/mol)
ECF	Electro-coagulation/flotation	F	Faraday's constant (96486C/mol)
EO	Electro-oxidation	v	Volume (m^3)
COD	Chemical oxygen demand	kL/h	kilolitres/hour
BOD	Biochemical oxygen demand	A/m^2	Current density
TKN	Total Kjaldal nitrogen	HRT	Hydraulic retention time
ppm	Part per million	DAF	Dissolved air flotation

INTRODUCTION

Water is a very limited natural resource and in many cases there is not enough supply of water of appropriate quality for industrial and domestic use. Many pollutants in water streams have been identified as harmful and toxic to the environment and human health. Strategies for ecological protection generally include the development of new or improved industrial processes that have no or minor effects on nature, and of processes for the treatment of inevitable waste. The tendency of the cost of water to increase, and the higher cost of effluent treatment due to the new restrictions on its discharge to the environment have induced industries to adopt programmes aiming at the minimization of water consumption and favouring the development of new methodologies for the optimization of these resources [1].

As the rivers, lakes and other water bodies are being continuously polluted and the potable water supply is insufficient in many places, there is an urgent need to develop more effective, innovative and inexpensive techniques for the treatment of wastewater. Conventional treatments of wastewater containing organic and inorganic compounds by coagulation and flocculation have been used for decades to destabilize the colloidal substances. In these processes, aluminum sulfate, ferrous sulfate, and ferric chloride have been used as coagulating agents and other additives (e.g. polyelectrolyte) are dosed to produce larger aggregates which can be separated physically. These are multi-stage processes that need repetitive supply of chemicals and extensive land area.

There is a need of more cost-effective methods to purify a wide range of polluted water on-site, and with minimal additives that are required for sustainable water management. Electrolytic treatment of wastewater presents an innovative technology in which a sacrificial metal anode and cathode produce electrically active coagulants and tiny bubbles of hydrogen and oxygen in water.

It is indicated that a variety of very promising techniques based on electrochemical technology, including EC, EF and ECF are more in use in wastewater treatment .According to Chen *et al.* [2] EC has many advantages over the conventional coagulation. Firstly, it is more effective in destabilizing small colloidal particles. Secondly, it is able to fulfill simultaneous coagulation and flotation with less production of sludge. Thirdly, the EC equipment is very compact and thus also suitable for installation where the available space is rather limited. Furthermore, the convenience of coagulants generated in wastewater by adjusting current that makes automation quite easy. Electrochemical treatment seems to be a promising treatment method due to its high

effectiveness, its lower maintenance cost, less need for labor and rapid achievement of results [3]. These remediation methods have been used as ‘‘niche technologies’’ where biological treatments are unsatisfactory [4]. Electrolysis offers prospective advantages of relatively simple equipment, oxidative or reductive chemistry, and operation at ambient temperature and pressure. Challenges include freeloading processes such as wastewater electrolysis that lowers current efficiency, formation of insulating deposits on the electrode surface and the need for inexpensive electrode materials for the wastewater treatment.

The “Electrolysis” literally means to break substances apart by using electricity. Michael Faraday first formulated the principle of electrolysis in 1820. The process occurs in an electrolyte, a watery or a salt melting solution that gives a possibility to transfer the ions between two electrodes. When an electrical current is applied, the positive ions move to the cathode while the negative ions move to the anode. At the electrodes, the cations are reduced and the anions will be oxidized. Environmentally oriented electrochemistry is more and more asked for pollution abatement of wastewater and reclaiming the requirement of discharge or permissible limit of wastewater. Under these circumstances an electrochemical treatment is an emerging technology with many applications in which a variety of unwanted dissolved toxic chemicals and microorganisms can be effectively removed from wastewater.

Lin *et al.* [5] explained that the mechanism of the electrochemical process in aqueous systems is quite complex. It is generally believed that there are three possible mechanisms involved in the process: EC, EF and electro-oxidation (EO). Electrolytic effluent treatment is based on the anodic dissolution of metals which form their hydroxides and the pollutants are removed by sorption, coagulation, and other processes occurring in the space between the electrodes [6]. Perng *et al.* [7] evaluated the pilot-scale study using pulsed electrocoagulation technology to treat the wastewater of an old corrugated containerboard (OCC)-based paper mill effluent. The technology was found to be effective for maximum removal of 47.7% of conductivity, 99.3% of suspended solids (SS) and 75% of chemical oxygen demand (COD) using current density of only 240 A/m and hydraulic retention time (HRT)of 16 min.

A pilot scale EC unit (supplied, commissioned and trialed by EC Pacific Pty Limited, Sydney) capable of treating approximately 10 kilolitres/hour (kL/h) was installed at Burrangong meat processors (BMP) in Young in May 2000. Trials were conducted to determine the unit’s performance in treating cooled, diluted stick water from the facility’s Low Temperature Rendering Plant. Initial focus during the first year was on establishing the best type of equipment to permit separation of the EC sludge from the treated effluent. Later studies (November 2001 – May 2002) addressed the operating parameters for best performance of the EC unit. There was a typical removal rate of PO_4 (70 – 90 %), Oil & Grease (90 – 95 %), TKN (50 – 65 %), Total suspended solids (TSS) (90 – 95 %) and COD (80 – 90 %).

Electro-coagulation

EC process is the electrochemical production of destabilization agents such as Al and Fe that bring about neutralization of electric charge for removing pollutants. Once charged, the particles bond together like small magnets to form a mass. This process has been proven to be very effective in removing contaminants from water and is characterized by reduced sludge production, no requirement for chemical use and ease of operation [9]. Al plates can be used as electrodes to produce Al^{3+} ions by connecting the plates to low power supply (PS), producing Al^{3+} ions which attract all the negatively charged particles especially the bacteria, causing their coagulation and sedimentation [10,11]. During EC, the coagulant is generated *In situ* by electrolytic oxidation of an anode of appropriate material. Charged ionic species are removed

from wastewater by allowing ions to react with oppositely charged ions, or with flocs of metallic hydroxides generated within the effluent [12]. Lai and Lin [13] investigated the EC of chemical mechanical polishing (CMP) wastewater from semiconductor fabrication. The study explored the feasibility of treating the CMP wastewater by EC to simultaneously lowering the wastewater turbidity, copper (Cu) and COD concentrations.
The EC technique has been observed to be more effective for the removal of COD than the conventional coagulation and sedimentation processes. Soluble metal electrodes like Al and Fe were found to be very effective in comparison to insoluble electrodes such as carbon (C), and titanium (Ti). Al and Fe ions support to the coagulation of colloidal particles [14]. In this method of treating polluted effluent, sacrificial anodes (Al and Fe) corrode to release active coagulant precursors into the wastewater. These molecules produce insoluble metallic hydroxides of Al and Fe which can remove pollutants by surface complexation or electrostatic attraction [15].

Electro-flotation
EF is also a method of separating substances in which electrically generated tiny bubbles of hydrogen and oxygen gas interact with pollutant particles making them to coagulate and float on the surface of water body [16]. Llerena *et al.* ([17] showed that the recovery of sphalerite fines was optimal at a pH range between 3 and 4. It was also observed that within this pH range, the hydrogen bubbles were smaller of about 16 ± 2 µm. At pH 6, the mean hydrogen bubble diameter was 27 µm. and at pH 2, the mean diameter of the hydrogen bubbles was about 23 µm when the current density was fixed at 500 A/m^2 using a 304 stainless steel wire mesh. A comparative study of EF system and dissolved air flotation (DAF) from soil washing water was carried out by Park *et al.* [18] to remove cadmium (Cd) ions. It was reported that much more Cd (100%) can be removed by EF using Al electrodes in comparison to DAF processes. Casqueira *et al.* [19] carried out a laboratory scale study of EF cell using a platinum gore (5 mm) anode and St mesh cathode. The results showed that it was possible to remove 96% zinc (Zn) by EF using sodium dodecyl sulfate (SDS) as collector in the stoichiometric ratio 1:3, current density of around 8 mA/cm^2 and an inlet pH of about 7.0.

Mansur and Chalbi [20] examined the effect of operating parameters such as current density, oil concentration, flotation time and coagulant concentration on the performance of the EF cell. The maximum change in percentage of oil removal was observed to be 99.5% with 40 min flotation time; 1000 mg dm^3 initial oil concentration; 120 A m^2 current density and 3.5% NaCl by wt +30 mg dm^3 coagulants. Nahui *et al.* [21] studied the EF cell using St cathode and dimensionally stable anode (DSA) with a composition of $Ti/Ru_{0.34}Ti_{0.66}O_2$. It indicated 99% removal of the oil using a current density of 19.40 Am^{-2} with an energy consumption of 0.167kw-hm^{-3}.

Electro-coagulation/flotation
ECF processes can be applied to a broad range of water and wastewater treatment systems. These are most effective in removing inorganic contaminants and pathogens. Because of their broad applicability, they have been used for groundwater and surface water remediation at their several sites [22]. Cora and Hung [23] conducted a bench scale study of ECF for the removal of wastewater with Cd ions. During the process, a cloud or blanket of finely dispersed gas bubbles was created with the help of two metallic electrodes (cathode/anode). The fine bubbles raise and attach to insoluble contaminant particles like metals or other organic substances. The other electrolytic products in the form of free radicals might also react with soluble organic matter and may cause considerable transformation. This performance tends to occur after several minutes of the treatment. The floated sludge was observed to accumulate in the upper portion of the reactor covering its entire cross-sectional area.

The study on ECF process to treat refinery wastewater and to remove emulsified oil from wastewater showed that wastewater treated with aluminum hydroxide formed by dissolution of Al anodes when hydrogen evolved at the cathode floats, the hydroxide flocs adsorbed the oil. The prime differentiator between pollutant removal by settling or flotation seemed to be due to the current density employed in the reactor [24]. Kolesnikov *et al.* [25] used EF process of electrolysis in a controlled waste stream. It worked by creating a cloud or blanket of finely dispersed gas bubbles that raised and attached to insoluble contaminant particles such as hard to treat metals or other organic substances. The technology is typically described as the combination of the processes of EF and electro-precipitation. The gas bubbles are formed by electrolysis of water in which hydrogen originates at a cathode and oxygen at the anode.

In France, an ECF system was joined together to study the membrane process (micro filtration) on the flux of municipal wastewater parameters. The experiments were conducted in a continuous mode with a 71 L electrolytic cell and 15 Al electrodes for the removal of COD, SS and turbidity from the municipal wastewater permeate using the hybrid process. It showed that a combination (hybrid process) of an ECF system with microfiltration could increase the removal efficiency [26, 27]. A combined process of EC and EF was used by Ibanez *et al.* [28] and they explained that the gas bubbles can carry the pollutant to the top of the solution where it can be more easily concentrated, collected and removed. The metallic ions reacted with the OH ions which were produced at the cathode. Insoluble hydroxides adsorbed the pollutants which were then removed by precipitation and flotation. A low current produced a low bubble density leading to a low upward momentum flux conditions that may encourage sedimentation over flotation [29]. Cora and Hung [23] built an ECF reactor to treat wastewater with heavy metals. In this study cadmium chloride was the source of metallic ions. It was defined that the ECF reactor was able to achieve metal removal efficiency of 90% to 99% at all the applied current levels (1, 3 and 6 amp) for 30 min.

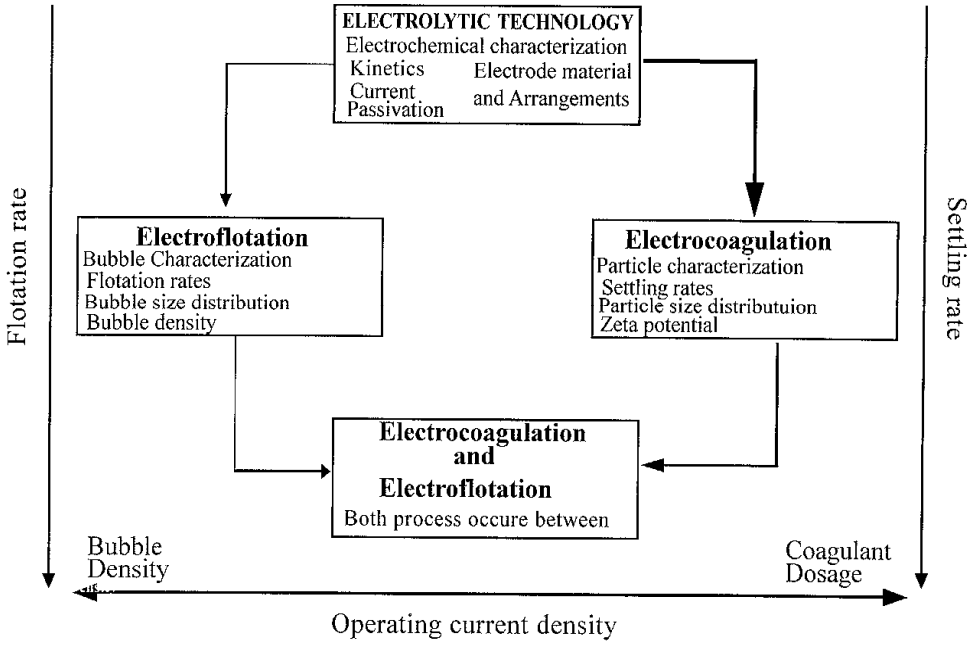

Fig. 1. Outline of electrolysis as an amalgamation technology.

The ECF technique offers an alternative method for removing pollutants from wastewater. This process involves applying of an electric current to sacrificial electrodes inside a reactor tank

where the current generates a coagulating agent and gas bubbles. In addition, it involves the electrolytic addition of coagulating metal ions directly from sacrificial electrodes. These ions coagulate with pollutants in the wastewater similar to that of the addition of coagulating chemicals such as alum and $FeCl_3$ and allow for easier removal of the pollutants by sedimentation and flotation [30].The removal efficiency of electrolytic processes with different electrodes and current density described by different authors is given in Table 1.

There are three main processes of Electrolytic technology viz. i) Electro-flotation, ii) Electro-coagulation iii) Electro-coagulation/flotation (Fig. 1).

Mechanism of electrolysis

Electrolysis is an electrochemical wastewater treatment technology that is currently experiencing both increased popularity and significant technical improvement. It is a complex process involving many chemical and physical phenomenon that use consumable electrodes to supply ions into the wastewater. In the process, the coagulant is generated *in situ* by electrolytic oxidation of Fe and Al electrode as an anode material which produces ions continuously in the system. The released ions neutralize the charges of the particles and thereby initiate coagulation. These ions may remove the undesirable contaminants (metal hydroxide and metal phosphate flocs generated within the effluent) either by chemical reaction and precipitation or by causing the colloidal materials to coalesce and are then removed by EF [31]. The subsequent values support the process of electrolysis given by different researchers in Table 1.

The main processes occurring during electrolysis are electrolytic reactions at the surface of electrodes, formation of coagulants in aqueous phase, adsorption of soluble or colloidal pollutants on coagulants, and removal by sedimentation and floatation. The main reactions at the electrodes are as follows [32]:

$$Al \rightarrow Al^{3+} + 3e^{-} \text{ (at anode)} \quad (1)$$

$$3H_2O + 3e^{-} \rightarrow 3 \; 2H_2 + 3OH^{-} \text{ (at cathode)} \quad (2)$$

The destabilized particles then aggregate to form flocs. In the meantime, tiny hydrogen bubbles produced at the cathode induce the floatation of most flocs, helping to effectively separate particles from wastewater. In addition, the cathode may be chemically attacked by OH^{-} ions generated together with H_2 at high pH values [33].

$$2Al + 6H_2O + 2OH^{-} \rightarrow 2Al(OH_4)^{-} + 3H_2 \quad (3)$$

Al^{3+} and OH^{-} ions generated by electrode reactions (1) and (2) react to form various monomeric species which finally transform into $Al(OH)_3$ according to complex precipitation kinetics [34].

Compared with traditional flocculation and coagulation, the EC in theory has the advantage of removing small colloidal particles. They have a larger probability of being coagulated because of the electric field that sets them in motion. Addition of excessive amount of coagulants can be avoided due to their direct generation by EO of a sacrificial anode. EC equipment is simple and easy to operate. There are several parameters such as size, shape and distance between electrodes, current density, conductivity, pH, reaction time which should be selected with care to optimize the process efficiency. Gurses *et al.* [34] investigated the effect of electrode nature, mixing, cell voltage, electrolysis time and current density on aqueous solutions of reactive dyes.

The principle of electrolysis is the cations generated by dissolution of sacrificial anodes which induce flocculation of the dispersed pollutants (Fig. 2).

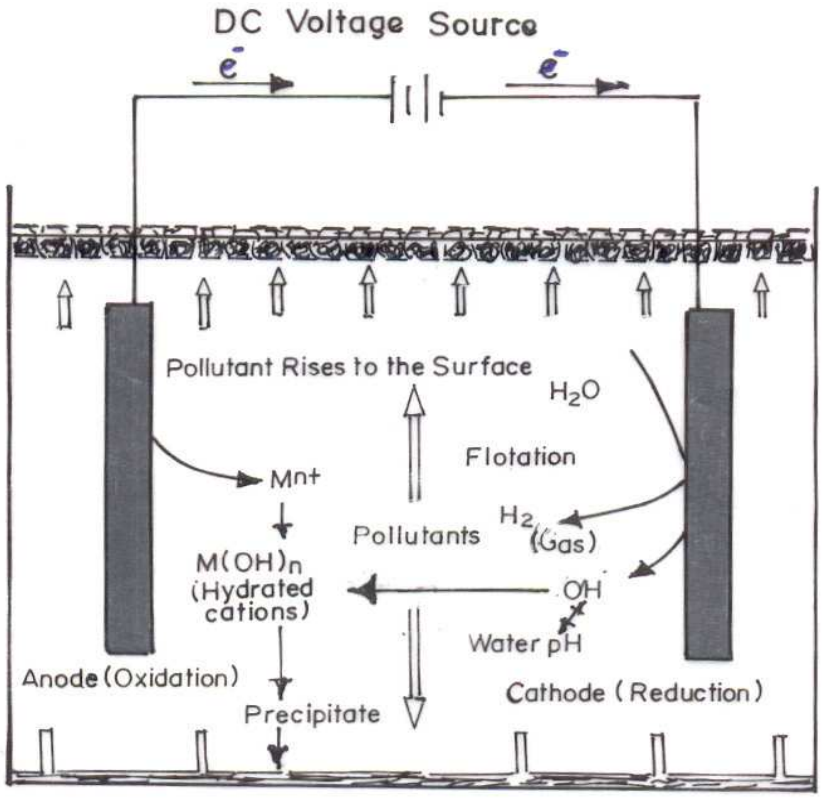

Fig. 2. Principle of electrolysis [35]

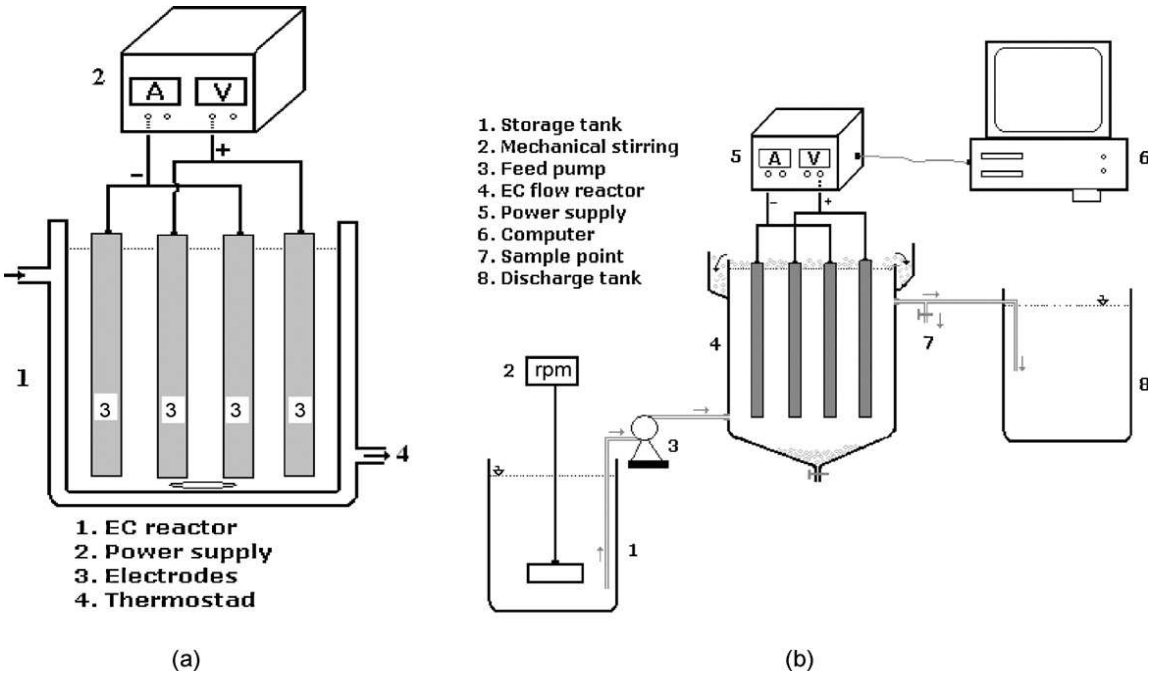

Fig. 3. Experimental setup for (a) batch and (b) continuous EC processes [31].

Factors influencing electrolytic treatment technology

The control, operation and chemical interactions of the electrolytic system affect the performance and reliability of electrolytic treatment technology. Adding to complexity and the

suitable contaminant removal mechanisms and their interactions with the reactor design, current density, electrode type and operating time influence the electrolysis.

Reactor design

The reactor design affects operational parameters including bubble path, flotation effectiveness, floc-formation, fluid flow regime and mixing/settling characteristics. It is important to design the reactor for a specific process and the reactors for energy conversion and electrochemical synthesis will have different drivers to those used in the destruction of electrolyte-based contaminants. The form of the reactants and products; and the mode of operation (batch or continuous) are also the important design factors (Fig. 3).

Desirable factors in reactor design and their implications include i) reasonable expenditure of low-cost components, a low cell voltage, and a small pressure drop over the reactor, ii) convenience and reliability in operation designed for facile installation, maintenance, and monitoring, iii) appropriate reaction manufacturing with in the reactor (homogeneous and suitable values of current density, electrode potential, mass transport, and flow), iv) simplicity and flexibility in an elegant design, which is attractive to end users [36].

Applied current density

Applied current density plays significant role in electrolytic treatment as it is the only operational parameter that can be controlled directly. In this system electrode spacing is fixed and current is a continuous supplied. Naohide *et al.* [37] treated dyestuff using PbO_2 anode and reported that Orange II was decolorized completely by a 120 min electrolysis procedure using a PbO_2 anode at current density of 0.2 A/cm^{-2}. After destabilization of the colloidal suspension, effective aggregation requires adequate contact current and more coagulant (Al) available per unit of time The residence time is decreased in the reactor, reducing the probability of collision and adhesion between pollutant and coagulant [29,38]. Current density directly determines both coagulant dosage and bubble generation rate; and strongly influences both solution-mixing and mass-transfer at the electrodes [15].

Kashefialasl *et al.* [39] evaluated the bench scale study of dye removal (Acid yellow 36). There was a maximum dye removal of 83.5% at the 127.8 A/m^2 for 6 min. from the initial 50 mg/l dye concentration. Kalyani *et al.* [40] ascertained the maximum color removal 92% and 84%; and COD 95% and 89% using mild St and Al electrodes respectively at $10mAcm^{-2.}$ This was attributed due to the fact that at high current densities, the extent of anodic dissolution increased and in turn the amount of hydroxo-cationic complexes resulted in increase of the color and COD removal (Fig.4).

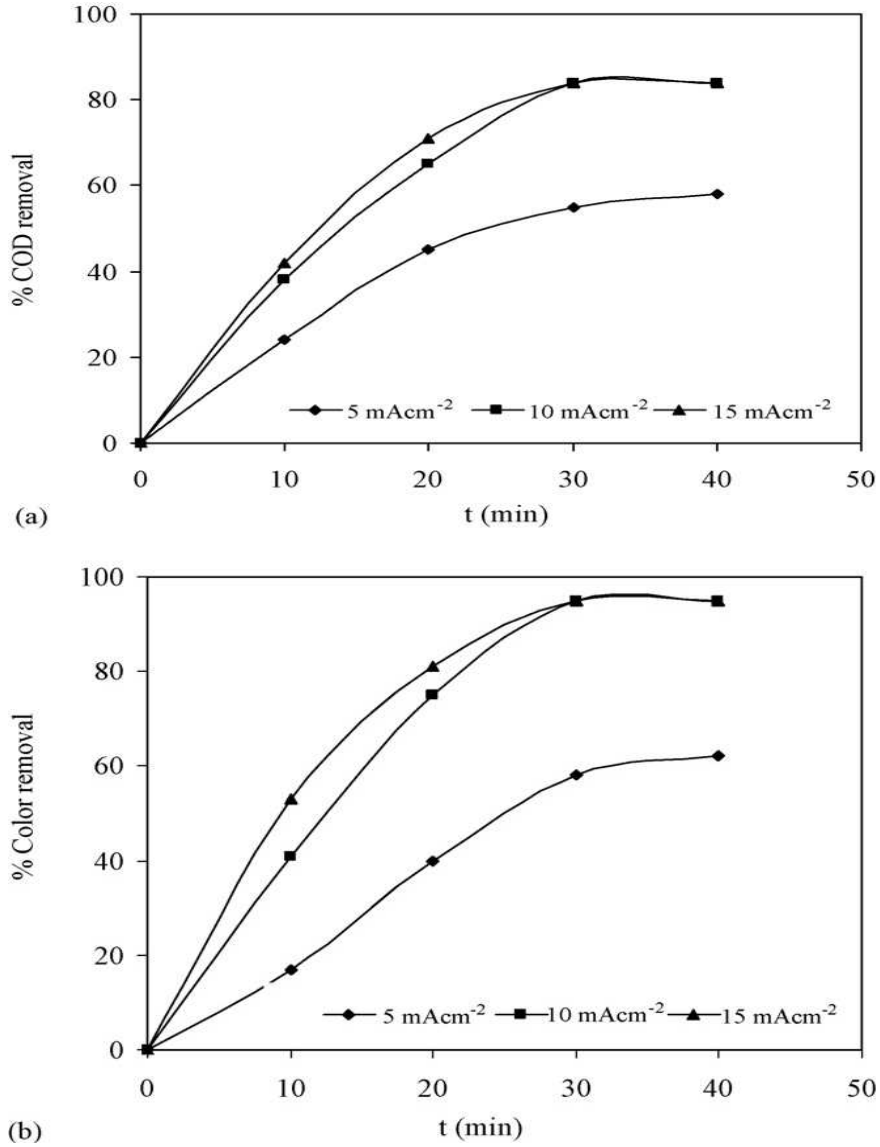

Fig. 4. Influence of applied current density (a) percentage COD removal, (b) percentage colour with electrolysis time, anode: Al; pH: 5; NaCl: 400 ppm; influent concentration: 3200mg l^{-1} [40].

Kobya *et al.* [31] investigated the bench and continuous scale study for phosphate and zinc removal from ZPO (zinc phosphate) rinse water. It was found that the optimum operating conditions for removal of PO_4 and Zn were current density of 60.0A/m^2, pH 5.0 and operating time of 25 min with Al electrode; and current density of 60.0A/m^2, pH 3.0 and operating time of 15 min with Fe electrode. The highest PO_4 and Zn removal efficiencies at optimum conditions were 97.7% and 97.8% for Fe electrode and 99.8% and 96.7% for Al electrode. Removal efficiencies of PO_4 and Zn were found to decrease when flow rate was increased from 50 to 400 ml/min in continuous mode of operation. This was due to the fact that the amount of anodic dissolution of Al and Fe electrodes increased by high current densities resulting in a greater amount of precipitate for the removal of pollutants [41].

Electrode type and arrangement

The wastewater to be treated is passed through the electrolytic reactor with electrodes and was subjected to coagulation and flotation by generating the ions forms the electrodes. These ions floating on the surface of wastewater after being captured by hydrogen gas bubbles are generated at cathode surfaces. The electrode connections in an electrolytic reactor are monopolar and

bipolar. A simple arrangement of the electrode connections in the electrolytic reactor is shown in Fig.5. Cell voltage and current are measured as digital and need to be controlled in all these experiments. With monopolar connections, an electric potential is connected between 'n' pairs of anodes and cathodes [42, 35]. Parallel connections to each electrode cause current (I_0) to pass across each electrode and solution but if an electrical potential (U_0) is applied between two feeder electrodes, a series of connections to bipolar electrodes cause the same current to pass through ''n'' electrode pairs.

Ciardelli and Ranieri [43] performed a laboratory scale study on wastewater of different characteristics (from finishing and dyeing processes, plant wastewaters before and after active sludge treatment) with electrochemical treatment with constant current and alternate Al and Fe electrodes. It was found that there was maximum COD, chlorides (Cl) and sulphate (SO_4) removal of 80%, 75% and 55% respectively. Kobya *et al.* [44] demonstrated the bench scale study of the textile wastewater and found that the Fe was more efficient than Al electrode in COD removal. The results indicated that in acidic medium pH < 6, COD and turbidity removal efficiencies of Al electrodes were higher than those of Fe, while in neutral and alkaline medium Fe was preferable. On the other hand, for the same turbidity or COD removal efficiencies, Fe required a current density of 80–100 A/m^2, while Al required 150 A/m^2 for a operating time of 10 min. Rahmani [45] carried out a laboratory scale study for the removal of turbidity at 20V. It was found that in 20 min, the removal efficiency for Al, Fe and St electrodes was 93, 91 and 51 % respectively. Based on turbidity removal efficiency, Al was more efficient electrode materials prior to Fe and St as sacrificial electrode.

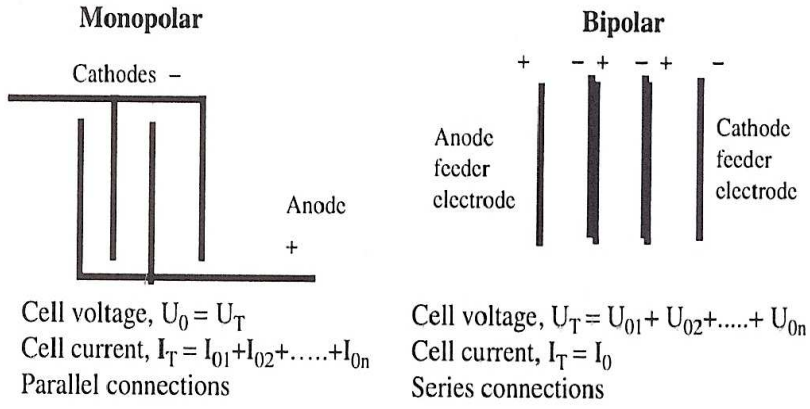

Fig. 5. Monopolar and bipolar electrode connection [42]

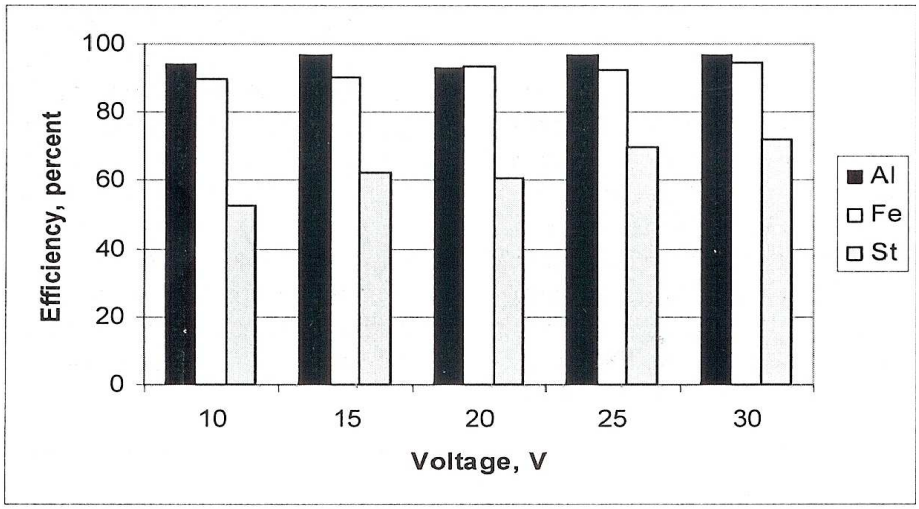

Fig. 6. Comparison of turbidity removal rate of different electrode [45]

Vlyssides *et al.* [46] conducted a number of experiments in a laboratory scale pilot plant using Pt/TiO_2 anode in presence of NaCl as a supporting electrolyte. It was explained that the 89% COD removal. The treatment efficiency depended on the catalytic activity of the anodes used, the COD loading rates and the pH of the solution.

Manisankar *et al.* [47] studied the effect of halides (NaF, NaCl and NaBr) in the electrochemical treatment of distillery effluent using anodized graphite plate anodes and graphite cathodes. They observed complete decolourization in all cases. A maximum of 93.5%, biochemical oxygen demand (BOD), 85.2% COD and 98.0% absorbance reduction were obtained in the presence of NaCl as supporting electrolyte.

According to Walsh [48] certain harms occurred related with electrodes and its stability viz. a) activity and surface area changes due to catalysis, blockage, and potential-distribution, b) adsorption/desorption of reactant, product, intermediates, contaminants, c) film formation/removal via e.g., passivation or polymerization, and d) Phase transformation e.g. solid–solid, intercalation and dehydration.

Operating time duration

Generally, the organic concentration in wastewater reduces with the increase in electrolytic time. Ni'am *et al.* [49] studied the effect of time at constant current density of 5.62 $mAcm^{-2}$ and observed that the removal of COD and turbidity as a function of operating time changed from 10 to 50 minutes, there was a removal of COD 15.17% to 76.57% and turbidity 9% to 98.2 %. Zayas *et al.* [50] studied the effect of electrolysis time on the purification of vinasse biological treated + coagulation/flocculation (BT +CF) at different pH values (4.1, 5.0 and 7.0) was studied at constant cell potential (5 V) and analyzed (Fig. 4). Removal of COD, colour and turbidity as a function of pH after 20 minutes of electrolysis of vinasse BT +CF with a cell potential difference of 5V, the removal percentage of COD increased linearly between 10 and 30 min, but from 40 min onwards attained a constant value of 99%. By contrast, the samples with initial pH values of 5.0 and 7.0 attained 99% removal of COD after 65 min of electrolysis, that is, 25 min later than the pH 4.1 sample. However, in the electrolysis time interval of 20 min $\leq$te $\leq$65 min, the removal percentage of COD at a given electrolysis time was always higher at pH 5.0 than at pH 7.0. These findings suggested that at pH value around 7.0, the degradation of organic material in vinasse BT +CF via EO is less favored, and hence longer electrolysis times are necessary to obtain maximum efficiency of removal.

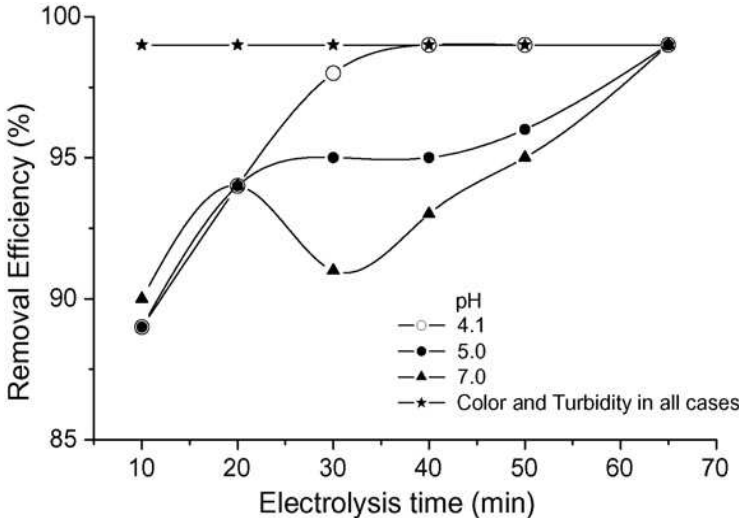

Fig.7. Removal of COD, color and turbidity as a function of electrolysis time during electrochemical treatment of vinasse BT +CF with a constant cell potential difference of 5V [50].

Sengil *et al.* [51] studied the bench scale treatment of tannery liming drum wastewater. The removal efficiency of the parameters depends directly on the concentration of hydroxyl and metal ions produced on the electrodes. After 10 min of electrolysis, COD, sulphide and oil–grease removal efficiency at pH 3 and 7.85 mA/cm^2 current density were 65.7%, 62.5% and 91.4%, respectively. Gao *et al.* [52] investigated the ECF technology for treatment of algae. The results indicated that Al was an excellent electrode material for algae removal as compared with Fe. The optimal parameters determined were: current density = 1mA/cm^2, pH= 4–7, water temperature = 18–36 ◦C, algae density = 0.55×109–1.55×109 cells/L. Under the optimal conditions, 100% of algae removal was achieved with the energy consumption as low as 0.4kWh/m^3.

Operating cost of electrolytic treatment

The process of evaluating and selecting appropriate wastewater treatment technology usually begins with a technical feasibility study that depends on the nature of the application. The most important aspect that should be considered to estimate the capital investment of a treatment of any technique, as stated by Faraday's law, the consumption rate of an Al anode is linearly proportional to the current and the electrolysis time. However, in accordance with the results obtained by Chen *et al.* [11], the actual electrode consumption may be reduced or increased from the theoretical value depending upon the wastewater characteristics and operational conditions due to the electrochemical side reactions. According to Kumar *et al.* [53], the EC process offers the possibility of anodic oxidation and *in situ* generation of adsorbents (such as hydrous ferric oxides, hydroxides of aluminum). The electrode material has a significant effect on the treatment efficiency, in terms of both cost and removal of polluting compounds and, if the treated water is destined for human consumption, this material can not be toxic. Although Fe, Al and St electrodes are inexpensive and easily available, they are anodically soluble, leading to high wear and thus generating sludge.

The operating cost (OC) involves costs of chemicals, electrodes and energy consumptions as well as labor, maintenance, sludge dewatering and disposal, and fixed costs [54]. According to Kobya *et al.* [31], energy and electrode material costs were taken into account as major cost items in the calculation of the OC (US$/m^3). The energy consumed was estimated at a cost of

0.12 US$/kWh (a). The Fe electrode consumption was estimated at a cost of 0.60 US$/kg (b), whereas a cost of 2.4 US$/kg was considered for the Al electrode material.

$$\mathbf{OC = a\ C_{energy} + b\ C_{electrode} + c\ C_{chemicals}}$$

Where C_{energy} (kWh/m^3) and $C_{electrode}$ (kg Al or Fe electrode/m^3) are consumption quantities for treatment of the ZPO rinse water. Cost with respect to electrical energy (kWh/m^3) was calculated as:

$$\mathbf{C_{energy} = U\ I\ t\ EC\ /V}$$

Where U is cell voltage (V), I is current (A), t EC is the time of EC and V is the volume (m^3) of the ZPO rinse water. The costs of energy are extremely dependent on the currency of particular country. Cost for electrode (Kg Al/m^3 wastewater) is calculated by the following equation by Faraday's Law:

$$\mathbf{C_{electrode} = \frac{ItM_w}{ZFv}}$$

Where, I is current (A), t is time of electrolysis (s), MW is molecular mass of Al (26.98 g/mol), z is no of electron transferred (z = 3), F is Faraday's constant (96487C/mol) and v is volume (m^3) of wastewater (Table 2).

Table1. Summary of pollutant removal efficiency by electrolysis

Reference	Pollutants	Cell voltage (V)	Current or Current density	Electrodes Connections	Removal path	Treatment Efficiency (%)	Reactor
Alfafara *et al.*, [55]	P, Algae from eutrophied lake water		80–430 Am^{-2}	Al/ titanium alloy Or C anode	Electro flocculation And EF	40–50	Batch and continuous
Bektas *et al.*, [56]	Boron	0–30	0–5 A	Al	EC	92–96.	continuous
Buzzini *et al.*, [57]	COD and Colour		19, 38 and 76$mAcm^{-2}$	Al	EC	67-98	continuous
Daneshvar *et al.*, [58]	Brackish water: hardness, SO_4^-, Cl^-		22 Am^{-2}	Fe and st	Floated and settled	40–90	Continuous
Dimoglo *et al.*, [59]	COD , turbidity Phenol, Hydrocarbon and grease		5 to15 mA cm^{-2}	Al/Fe; Graphite/St steel mesh	EF and EC	40-88	Batch
Kobya *et al.*, [44]	Textile wastewater COD	<30	5–20 $mAcm^{-2}$	Fe/Al- Monopolar	Floated and settled	90–99.5	Batch
Kobya *et al.*, [60]	COD	<30	200 Am_2	Al and Fe Monopolar	Floated and settled	65–93	Batch
Ni'am *et al.*, [49]	COD and Turbidity		3.51 to 5.62 mA cm^{-2}	Fe	EC	65 - 95	Batch
Kalyani *et al.*, [40]	Colour, COD		10$mAcm^{-2}$	Al and mild steel	ECn	84-95	Batch
Pouet and Grasmick [27]	Municipal wastewater: COD	0–80	0–40 A	Al/Al- Plate	Settled and floated with DAF	70–80	Continuous
Rahmani AR.[45]	Turbidity	10-30		(Al, Fe and St)	EC	51-93	Batch
Ugurlu [61]	Nitrite, nitrate, and ammonia	12	40–80 mA	Al and Fe electrodes	Electro-reduction and EC	65–95	Batch

Table 2. Energy and operational facts between CP and EC [62]

Parameter	Chemical Precipitation	Electro-coagulation
Effective flow rate	12.5 l/h	12.5 l/h
Annual capacity	110 m^3/y	110 m^3/y
Material used	Sodium liquor (NaOH)	Al plates (Al)
Material cost	0.36 US$/l (NaOH-1M)	5.75 US$/kg (Al-plates)
Material used / m^3	40 l (NaOH-1M) / m3	1 kg (Al) / m3
Material cost / m^3	14.37 US$/$m^3$	5.75 US$/$m^3$
Annual material cost	1581.05 US$/y	632.23 US$/y
Energy demand	60 Wh (agitator, pump)	125 Wh (EC-reactor)
Energy demand / m^3	4.8 US$/kWh/$m^3$	10 US$/kWh/$m^3$
Annual energy cost	152.32US$/y(0.28 US$/kWh)	316.02US$/y(0.28 US$/kWh)
Annual treatment cost	1,732.37 US$/y	948.21 US$/y
Treatment cost / m^3	15.21 US$/$m^3$	8.62 US$/$m^3$

Thus, it is easy to classify a general mechanism of Electrolytic technology and their affecting parameters (reactor geometry, current density, time and electrode type and arrangement) so as to understand the wastewater treatment processes. This will help in focusing attention on electrolytic treatment as a feasible wastewater treatment technology in the near future.

CONCLUSION

Electrolytic technology is an essential and significant discipline in many sectors of wastewater treatment including clean synthesis, monitoring of removal efficiency of contaminants, water sterilization, clean energy conversion and also the efficient storage and utilization of electrical energy. Electrolysis has significant advantages such as its simple equipment, convenient operation and non-requirement of chemical substances for the sedimentation and floc generation. It allows the wastewater treatment to electrochemically oxidize or reduce the organic contaminants to non-hazardous inorganic substances. Among various electrolytic processes, the

EC seems to be the best compromise as the process is technically simpler, with no chemicals, which are of high cost in comparison to the electrodes. The technology has potential for wastewater treatment where surface water or groundwater is normally contaminated. The research work should be focused on quantifying the interactions between electrolytic processes and their feasibility in terms of the development of advanced electrode materials, application of different electrodes types, developing the more refined and optimal design for electrolytic reactors, energy consumption and the economy so that the technology can be an effective, low cost and eco-friendly alternative process for the removal of various recalcitrant contaminants from wastewater. Such technology can be helpful in recycling /treatment of the wastewater for producing high quality water at an affordable price.

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