

CHAPTER II
LITERATURE REVIEW

The electrolytic treatment of wastewater have appeared in the patent literature since 1889, and the first installations of importance for the electrolytic treatment of sewage were in London about 1890, but very little has been done on a large scale. A considerable amount of work was done on this process during the first quarter of this century, several demonstration plants were built, and resulted in the establishment of several electrolytic municipal and industrial waste plants. Some of the methods are described briefly as follows :

Webster process (MARSON, 1965) Wastewater was made to flow through channels a few inches wide lined with insulated iron plates, comprising of electrodes. The wastewater was electrolyzed at a potential of about 10 volts. If insufficient chloride were present to generate chloride, sea water or salt was added. Effectively, iron went into solution or a floc of ferric hydroxide entered the stream and caused rapid precipitation of the sludge and de-odorisation of the supernatant liquor. Consumption of iron was high, amounting to several pounds per 1000 gallons treated, and a very heavy and voluminous sludge was obtained. Webster battled to overcome disadvantages, but apparently nothing further was done.

Landreth process (MILLER AND KNIPE, 1965) This method treat raw wastewater with lime and electrolyzed it with iron electrodes. The idea was to purify the sewage with nascent oxygen, but at reasonable efficiencies

only about 10 ppm of oxygen was produced. This is insufficient to do more than deodorise the sewage. It was also claimed that the sewage bacteria were reduced by 99.4 % but the large lime dosage used would account for much of this by its flocculating action.

Hermite process (MARSON 1965) Hermite believed that the magnesium salts in sea water had a useful effect in treating sewage. He had done on electrolysing a mixture of sewage with a proportion of sea water or alternately, by electrolysing the sea water first and mixing with sewage. An electrolyser was used involving carbon anodes surrounding a revolving, platinum covered cylinders which was continuously wiped, to remove the deposit of magnesium carbonate building on it by interaction of dissolved CO_2 with the nascent $\text{Mg}(\text{OH})_2$ produced in the alkaline medium around the cathods. This is a powerful flocculant and brings down the sewage solids very quickly and effectively. At the anode active chlorine is produced, it is probable that ammonia and aminocompounds in the slightly alkaline sewage are converted to chloramines, which are much more effective disinfectants than hypochlorite in the presence of organic matter, and retain their activity longer. Oxygen is produced as well as chlorine at these dilutions, and is probably chiefly responsible for the instantaneous removal of smell.

Foyn process (MARSON 1965, POON, CALVIN AND BRUECKNER 1975) The electrolytic cell was set up to electrolyse a sewerage-sewage mixture. The anode is a series of graphite blocks laid on the vessel floor, and cathode is an

iron grid. Pure sea-water flows around the anode. Between the anode and the cathode is an interface separating pure sea water flowing along the bottom and the sewage-sea water mixture bathing the cathode. The chlorine produced is entirely dissolved in the lower layer, which is mixed with the effluent leaving the upper part. Dr. Foyen used the process to remove phosphate ions from sewage entering the Oslo fjord.

Mendia Process (MARSON 1965) In this process, the electrolytic cell is extraordinary simple; anode being a sheet of graphite laid on cell floor, cathode is an iron grid. Sea water-sewage mixture flows through the cell with a liquid depth of about 3 cm. The basic difference between this process and the other is that no chemical is added and the cell units are relatively simple.

However, all electrolytic treatment plants had been abandoned by about 1930. Estimates for relatively large systems indicated that the electrolytic method would cost about double that of conventional methods. This, it is felt, was the single biggest factor the method failed to gain more acceptance.

Recently, electrolytic treatment of sewage has been extensively reviewed by Marson (Ref. 17 and 18). Work has begun in Europe on the electrolysis of wastewater mixed with sea water. The object is to use compounds present in the sea water; hypochlorite is generated, and the magnesium salts present form precipitates that aid in sludge flocculation. To accomplish this, a source of chloride ions is needed, and these ions are usually added in the form of a salt or sea water. In the electrolytic process chloride ions are oxidized to chlorine gas which, in turn, oxidizes

the organic matter. Furthermore, the salt serves to increase the conductivity of the solution, thus reducing power costs to a reasonable level.

MARSON (1965) reported that electrolytic processes were capable of BOD removal of 71 percent and suspended solids removal of 100 percent in municipal wastewater. He also pointed out that the hydrogen gas liberated at the cathode forms small bubbles which carry the suspended solids to the surface of the solutions.

MILLER and KNIPE (1965) had investigated the possibility of using an electrolytic method for the removal, destroy, or render less objectionable the trace dissolved materials in wastewater effluent. Several types of electrolytic cells were used. Based on the studies, they reported that:

(1) The early electrolytic treatment using iron electrodes in a waste solution treated with lime was probably effective because of the relatively high pH and small amount of hypochlorite formed. There is no evidence that any organic material was decomposed by the electrolytic action.

(2) Electrolytic action may prove a very efficient way to introduce chemicals into wastewater. An eroding iron anode can introduce an iron floc uniformly and at a constant rate without the introduction of an anion. A lead dioxide anode can convert chloride ions in a waste solution to hypochlorite ion at a uniform and controlled rate without introducing any new materials into the solution.

(3) Iron, lead, magnesium, aluminum, graphite, and copper all erode when made anodic in secondary effluent, and can be used only under special conditions.

(4) Lead dioxide, platinum, and platinum-plated titanium do not erode when made anodic in secondary effluent.

(5) All electrode materials except lead dioxide worked satisfactorily as the cathode in secondary effluent.

(6) Graphite, lead dioxide, platinum, and platinum plated anodes generate significant amounts of hypochlorite when used in secondary effluent.

(7) Lead dioxide was shown to be the most effective anode material for the reduction of ABS, COD, and chloride in wastewater. It did not reduce total solids, suggesting that the treatment did not decompose the dissolved material into volatile material.

(8) Current density, initial pH, and temperature had little effect on the performance of lead dioxide.

(9) Graphite was attacked under all test conditions. But more severely at elevated temperatures and current densities.

(10) Electrolysis with a noble inert anode is very effective in the destruction of bacteria.

(11) The presence of hypochlorite ion in electrolyzed wastewater does not account for the reduction of ABS or COD, by the electrolytic treatment.

(12) The electrolysis of secondary effluent with lead dioxide anodes and platinum-plated titanium cathodes can reduce the COD by as much

as 80 percent, ABS by as much as 90 percent, and chloride by as much as 90 percent. Lead dioxide anodes with iron cathodes may be somewhat less efficient in reducing COD. All systems have little effect on total solids. CAMPBELL, WOODARD and HERER (1970) using electrolytic process for removal of color from draft pulp mill bleaching wastewaters. The electrolytic cell electrodes were composed of aluminum metal. Calcium chloride was used as the electrolyte. The electrolytic products were chlorine and polyvalent metal ions which might be effective in removing color from kraft pulp mill wastewaters. The thought being that the chlorine would be useful in decolorizing and that the polyvalent metal ions would aid in the coagulation. They reported that an ultimate color removal of 95 to 97 percent could be obtained within the range of applied current, namely, 1.2 to 7.2 amp. Furthermore, time required to obtain a given percent color removal varied inversely with the amount of current applied, 5 to 25 min, is required. POON and BRUECKNER (1975) used the electrolytic cell similar to the one that was used in Foyn's study, and they reported that;

(1) Orthophosphate removals were respectively to wastewater-sea water ratios and power supplies. The mechanism of removals was primarily due to $Mg(OH)_2$ flocs adsorption, and the precipitation of calcium phosphate.

(2) Most of the nitrogen (NH_2-N) removal occurred at a pH of 10 or above by breakpoint chlorination, and little or no NCl_3 , NO_3 was detected.

(3) BOD removal was essentially by the active oxygen species, and suspended solids removal was found to be paralleled to BOD removal.



(4) Disinfection of wastewater was complete within 40 min or more of treatment.

(5) To obtain an effluent quality equal to or better than a secondary effluent, the average power consumption is 4.5 kwh/1000 gal. EDMOND SMITH, (1972) reported that electrolytic process has proven to be able to cope with a variety of wastewaters. These waters are paper pulp mill waste, metal plating, tanneries, canning factories, steel mill effluent, slaughter house, chromate, lead and mercury-laden effluents as well as domestic sewage.

By passing the wastewater between two sacrificial electrodes, the colloids electrical equilibrium is disturbed and now these colloidal particles will start to collide and form large lumps and chunks. At the same time that this process is going on, fine bubbles of oxygen and hydrogen are being generated at the anode and cathode, respectively. These fine bubbles are tending to escape and they are entrapped in these colloidal particles and float them to the surface as a foam. Another process is being activated while the removal of the colloidal particles is being effected. The current is pumping electron ions out through the electrolyte and these ions start looking around for something with which to combine electrically and chemically. If the wastewater is loaded with phosphates, silicates, magnesium, and calcium, the sacrificial electrode will combine chemically with these constituents forming insoluble precipitants and can be removed in a settling chamber.