

An electrochemical sewage treatment process

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Electrolysis of mixtures of sea water and waste water from a secondary treatment plant has been studied; the current density and the inter-electrode gap were varied. The results show a fast elimination of phosphorus compounds under favourable conditions. The rate of nitrogen removal is dependent on the formation, and subsequent degradation, of chloramines. In order to avoid the diffusion of the anodic products to the cathode, diaphragms of different materials were used; the best results were obtained with a cellulose pressed diaphragm. The energy consumptions for a phosphorus removal of 40 and 60% were 0.075 and 0.1 kWh m⁻³ of treated sewage, respectively.

1. Introduction

In recent years, attention has been drawn to an uncontrolled development of undesirable algal growths in the Adriatic sea [1]. Research on this topic demonstrated that the major cause of the algal growth was the high concentration of inorganic phosphorus and nitrogen compounds in the sea [2]. In the north Adriatic the phosphorus and nitrogen which give rise to the algal bloom mainly come from the Po river, from natural drainage of agricultural lands and from the industrial and domestic sewage of about twenty million peoples living in the north of Italy [3].

In the south of the Adriatic sea, nutrients come from agricultural areas and industrial sewage from a vast expanse of coast [4]; therefore they are of secondary importance when compared to the nutrient input of domestic sewage and indeed, algal blooms are mainly observed close to the discharges of large communities. For this reason the eutrophication phenomenon of the south Adriatic sea appears to a large extent controllable by removing the fertilizing elements from domestic sewage before their discharge into sea water.

In the past the common opinion that waste water treatment by electrolysis was an expensive process has limited its application to situations where it is not possible to use other methods. More recently, however, this method has been applied with encouraging results [5]. The electrical power costs for the electrolytic treatment

of domestic sewage reported in the literature [5, 6], are largely dependent on factors such as the quality of the treated waste waters, the required degree of purification and the type and efficiency of the cell used.

The aim of the present research is to study the best conditions of current, voltage, and cell design, in order to minimize the electrolysis process cost for removing the phosphorus and nitrogen from secondary domestic sewage.

2. Apparatus and procedure

The experimental apparatus used in the electrolytic treatment of secondary waste water is shown in Fig. 1. The cell is essentially a reduced version of that used by Mendia in its continuous flow plant [5]. It consists of a 1 litre capacity glass cell, 170 mm long, 100 mm wide, and 60 mm deep. The anode is a graphite plate, with dimensions of 115 mm × 69 mm × 10 mm, laid on the vessel floor. The connection of the anode to the power supply is realized by two graphite rods, 1 cm in diameter, covered with a thin Teflon coating. The cathode is an iron plate 2 mm thick with dimensions of 88 mm × 70 mm. The cathodic plate with longitudinal holes spaced 2 mm apart, was jointed to the cover of the cell through a screw which allowed variation of the electrode gap in the range 0 to 35 mm. To avoid the mixing of the anolyte and catholyte, the anode and the cathode were divided by a diaphragm of pressed cellulose.

Both the anode and the cathode were connected

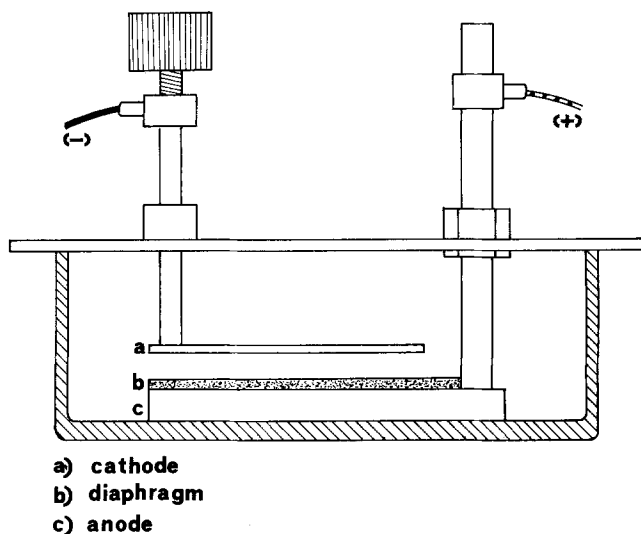


Fig. 1. The experimental cell used.

to a Systron Donner Md M5C 160-8A power supply which permitted regulation of the current in the range 0 to 8 A. In all experiments, voltage and current were monitored by a voltmeter and an ammeter connected in parallel and in series to the power supply unit respectively.

The electrolytic solutions used were mixtures of waste water and sea water. The waste water employed was synthetically prepared and reproduced the effluent of the Bisceglie biological sewage treatment plant whose composition is given in Table 1. In addition, the sea water used was a synthetic electrolyte prepared by dissolution in pure water of NaCl, MgSO₄, and CaCl₂ salts, in such amounts as to approximate the concentration of Cl⁻, Mg²⁺, and Ca²⁺ ions in sea water (see Table

Table 1. Chemical characteristics of effluent from Bisceglie secondary sewage treatment plant.

Species	Concentration (mg l ⁻¹)
Chlorides	442.2
Bicarbonates	552.2
Sulphates	144.2
Phosphates	28.8
Nitrates	93.0
Suspended solids	15.0
Ammonium	66.7
Potassium	66.8
Calcium	80.2
Sodium	376.6
pH	8.3

2). The mixing of the sea water and waste water was carried out a short time before their passage into the cell. The volume of the electrolytic solution treated changed with the electrode gap since the water-level was maintained constant 1 cm above the cathode.

During the experiments, samples were withdrawn at intervals by means of a syringe; the solution was filtered and the pH, orthophosphate, ammonia, nitrate, and total chlorine concentration were determined. The pH measurements were made using a Radiometer M51 pH meter. The orthophosphates were determined using the ascorbic acid colorimetric method [7]. Ammonia nitrogen was determined by the Nessler method [8]. The nitrates were reduced to nitrites with Zn in acid solution and then measured spectrophotometrically [9]. Free and combined available chlorine were determined by amperometric titration [10]. All colorimetric determinations were made using a Zeiss mod. PMQ II spectrophotometer and 1.0 cm lightpath.

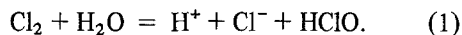
During electrolysis the following reactions take place:

(a) at the anode the chloride ion present in solution is oxidized to chlorine gas, which

Table 2. Chemical composition of synthetic sea water.

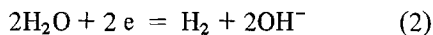
Cl ⁻ (mg l ⁻¹)	Mg ²⁺ (mg l ⁻¹)	Ca ²⁺ (mg l ⁻¹)
19 000	1 200	400

partly reacts with water molecules, according to reaction:



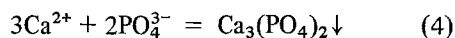
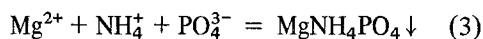
As a consequence of Reaction 1 the anodic solution becomes acid.

(b) at the cathode



is responsible for the pH increase and consequent precipitation of the magnesium ions.

According to Foyn [11], the presence of phosphates and ammonia in alkaline solutions (pH = 10), gives rise, in addition to the elimination of magnesium as $\text{Mg}(\text{OH})_2$, to the precipitation reactions



which are responsible for the phosphorus and nitrogen removal from the electrolysed water.

The observation that in some experiments the solubility of the MgNH_4PO_4 salt, expressed as phosphorus, is greater than the phosphorus initially present in solution induced Rohlich [12], and subsequently Poon and Bruecker [13], to postulate that the phosphate removal is mainly due to absorption onto $\text{Mg}(\text{OH})_2$ flocs rather than to the precipitation of the MgNH_4PO_4 salt.

The electrolysis in a cell where the cathode and the anode are separated by a diaphragm enhances the formation of alkaline conditions near the cathode. This fact is evident if one considers the data of Table 3. The experiments reported in this table were carried out with a current density of 3 A; with a 3 cm electrode gap and an electrolysis time of 30 s. The measurements have been made with diaphragms of the following characteristics:

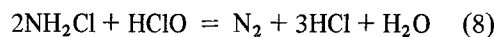
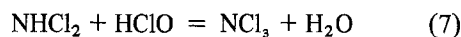
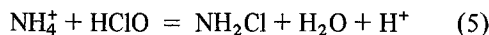
(a) a commercial asbestos plate 3 mm thick;

(b) cellulose acetate membrane 0.1 mm thick and with pores 0.1 μm diameter;

(c) cotton cellulose pure fibre pressed plates 0.5 μm thick and with pores of 2 μm diameter.

A survey of the data of Table 3 shows that the applied voltage remains approximately constant, and equal to about 12 V except when a diaphragm of asbestos is used; then to assure the desired current, 16 V potential difference must be applied. During electrolysis the asbestos, and to some degree also the cellulose, crumble easily so that a diaphragm of pressed cellulose has been used in this work.

The mechanism for the removal of nitrogen compounds [13] seems to be via the formation of chloramine and subsequent degradation through the reactions:



which take place at different pH values and concentrations of chlorine.

3. Results and discussion

In preliminary experiments electrolysis conditions (current density and electrode distance) were varied and it was observed that in many cases no $\text{Mg}(\text{OH})_2$ precipitate formed at the cathode because of inadequate pH variation owing to diffusion to the cathode, of chlorine and products of Reaction 1, which reduce the pH in the cathode region. The effect is particularly marked in our experiments since the waste water employed coming from the secondary treatment process, is lacking an adequate organic content to act as a

Table 3. Applied voltage, pH values, percentage phosphorus removal with the different diaphragms used. (Electrode distance = 3 cm; current density = 3 A; electrolysis time = 30 s).

	Without diaphragm	Asbestos	Cellulose membrane	Pressed cellulose diaphragm
Voltage (V)	11.5	16	12	11.5
pH	8.7	10.6	9.7	10.0
% P removal	8	45	38	42

Table 4. Percentage phosphorus removal with time, at various currents and electrode distances.

	Current (A)	30 s	1 min	2 min	5 min	10 min	30 min
$d = 1$ cm	1	40	50	52	58	62	70
	1.5	43	60	80	84	90	95
$d = 2$ cm	1.5	40	57	78	87	98	99
	2	61	71	87	89	96	99
$d = 3$ cm	2	33	52	56	67	88	96

reactive filter for the anodic products. For this reason all further measurements were carried out with a diaphragm cell. The results show that, while in experiments without a diaphragm the pH value near the cathode never exceeds 8.7, with the diaphragm the pH was 9.5 after a few seconds and, depending on the electrolysis conditions, lies between 9.5 and 11 in the following 40 min.

3.1. Phosphorus removal

The quantity of phosphorus removed is reported in Table 4 and Fig. 2, as functions of time, current density and electrode gap. A comparison of the results of Fig. 2 and data for the electrolytic treatment of sewage coming from primary

plant appears interesting. The data refer to measurements made in cells of 25 litre volume and an electrode gap of about 30 cm; under these conditions the reported phosphorus removal was, at best, 10% after 10 min and 98% after 1 h. Compared with these results, Fig. 2 shows that the average phosphorus removal was 45% after 30 s and 85% after 10 min; the last figure corresponding to a residual phosphorus content of 0.6 ppm.

In Table 5, the phosphorus removal after 30 s as a function of the applied voltage, current density, and electrode gap is reported. The data refer to a sea water/waste water ratio of 1/5. Looking at this table it appears that, at constant current, the applied voltage is influenced only

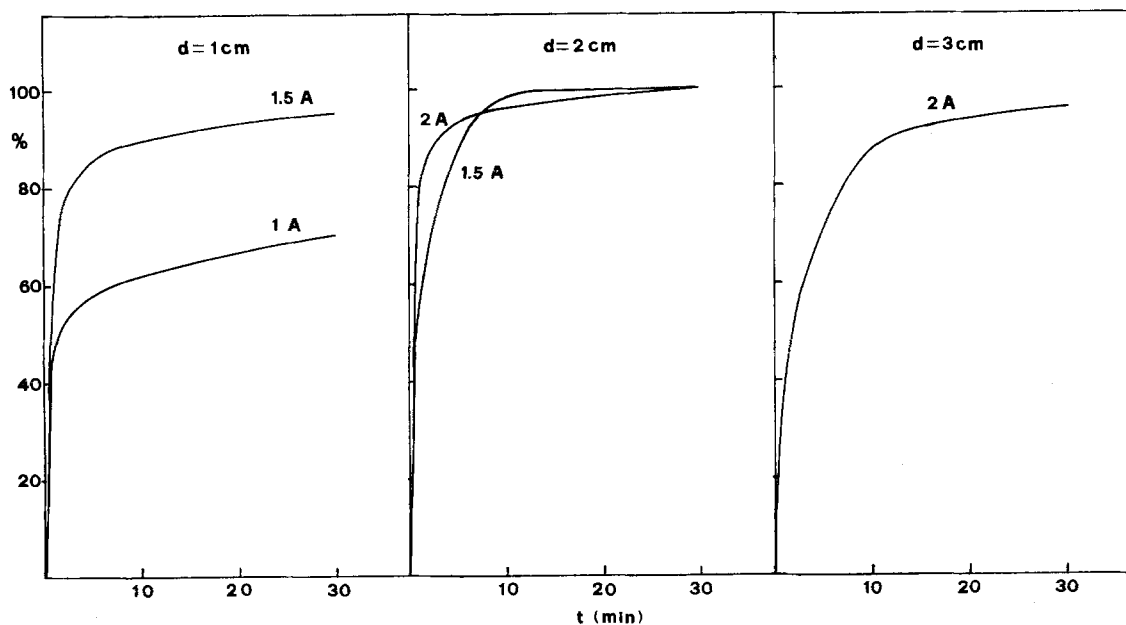


Fig. 2. Percentage of phosphorus removed against time, at different electrode distances and current densities.

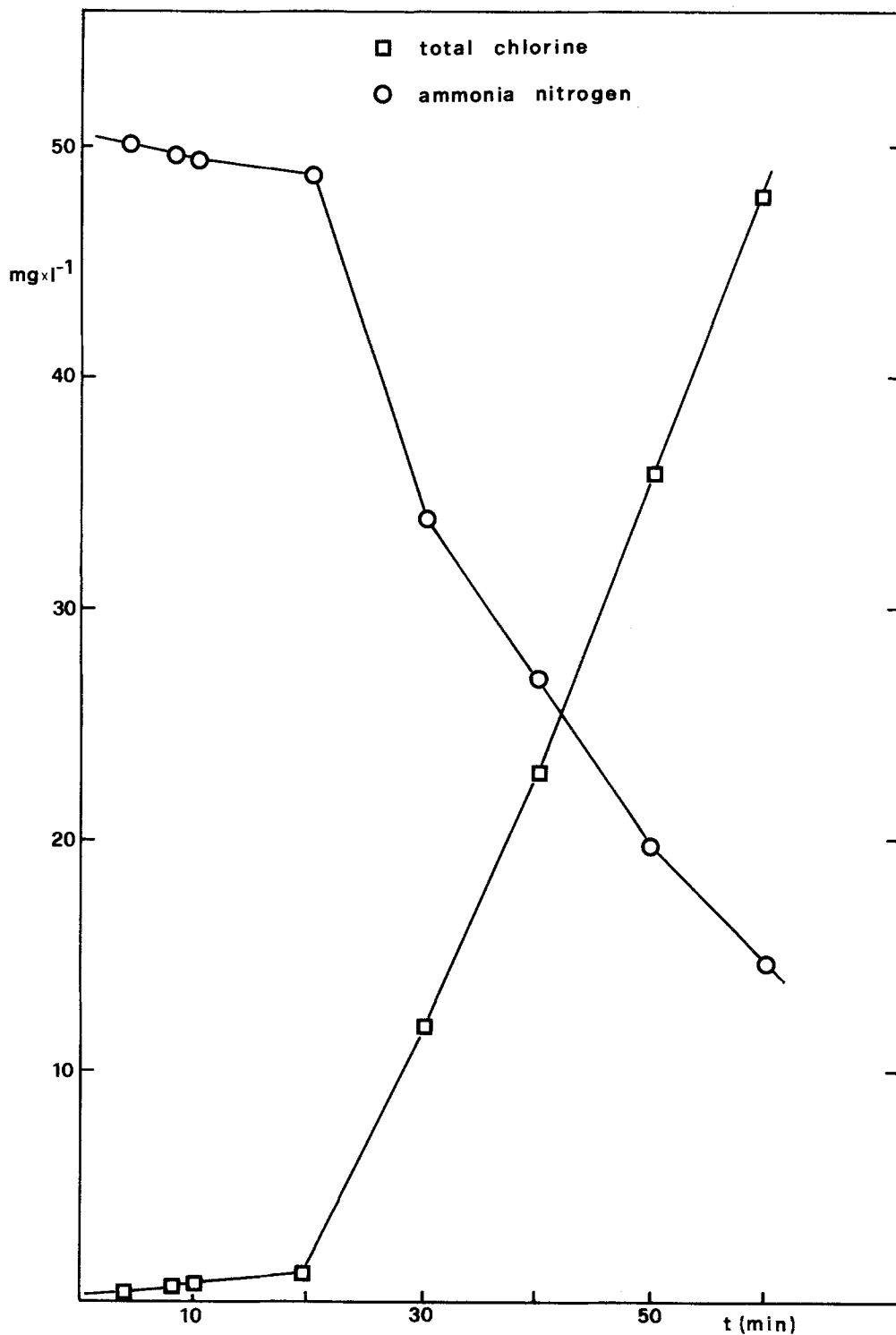


Fig. 3. Ammonia nitrogen; free and combined chlorine concentrations against time.

Table 5. Phosphorus removal at various currents, voltages, and electrode distances (electrolysis time = 30 s)

<i>d</i> (cm)	<i>I</i> (A)	<i>V</i> (V)	% P removal
3	1	6	30
3	1.5	7	33
3	2	7.8	33
3	3	11.5	42
3	4	18.5	50
2	1	5	30
2	1.5	5.5	40
2	2	6.7	61
1	0.5	3.7	15
1	1	4.5	40
1	1.5	5.7	43
1	2	6.2	45

slightly by the electrode gap indicating that the ohmic drop through the electrolytic solution is a small part of the applied potential difference. As expected, the percentage of phosphorus removed increases, with increasing charge passed. But, while at a distance of 2 cm doubling the current from 1 to 2 A also doubles the percentage of phosphorus removed, with 1 and 3 cm gaps doubling of the current causes only a very small increase in the phosphorus removed.

It can be observed that with current densities of 1 and 1.5 A the highest percentage of P removal is obtained at 1 cm; on the other hand, with a density of 2 A an electrode gap of 2 cm gives the best result. It should be noted that, in all cases, a distance of 3 cm gives the smallest percentage of P removed, a surprising fact which needs more investigation to be explained.

Table 6 reports the percentage of P removal obtained as a function of the ratio sea water/waste water; in these experiments the electrode gap and the current density used were 1 cm and

Table 6. Applied voltage and percentage phosphorus removal with different sea water/waste water ratio (*R*) (electrode distance = 1 cm; current density = 1 A; electrolysis time = 1 min)

<i>R</i>	<i>V</i> (V)	% phosphorus removed
1/3	4.3	57
1/5	4.5	50
1/9	4.7	15

1 A, respectively. Poor results are obtained with a ratio of 1/9; the percentage of P removal obtained using a 1/3 ratio is slightly better than that obtained with a ratio of 1/5; the volume of solution to be treated, however, increases and makes the use of the 1/5 ratio more convenient.

The results of experiments made at electrode distances smaller than 1 cm and with current densities smaller than 1 A give too low values for the percentage of P removed.

3.2. Nitrogen ammonia removal

Fig. 3 reports the concentration of ammonia and total chlorine against time. To understand these experimental results it is necessary to make reference to the experiments of Poon and Bruecker [13]. These authors, using an apparatus and electrolysis conditions previously described, noted that the concentration of combined chlorine begins to increase after 20 min and reaches a maximum value after an electrolysis time of 40 min. At this time the concentration of ammonia present in solution is very small; free chlorine, through Equation 1, generates HClO which in turn reacts, according to Equation 8, with monochloramine giving free nitrogen and acid conditions. As a consequence of these facts, after an electrolysis time of about 1 h, the cathode region has no ammonia and combined chlorine, has an high concentration of free chlorine and pH values are inclined to decrease.

In our experiments the initial ammonia concentration was high (50 ppm compared with the 10 ppm of the Poon experiments); in addition, the presence of a diaphragm hinders the migration of free chlorine towards the cathode. The consequence is that in the first 20 min the ammonia removed is a small percentage of the initial value, as shown in Fig. 3. After 40 min the ammonia is reduced to 50% and reaches 35% in 60 min. The fact that in our experiments the ammonia concentration is not zero even after an electrolysis time of 1 h, is partly explicable by the presence of the diaphragm which in some way hinders the diffusion of Cl₂ and related products. It is also possible that nitrates present in solution in high concentrations reduce at the cathode, thus supplying the ammonia which Reaction 8 eliminates.

3.3. Economics

A comparison between the costs of the various processes reported in the literature, is difficult because of the composition difference of the input sewage and output from the cell. The most important processes in the literature discuss the treatment of raw waste water. Foyn reports that the amount of electricity necessary for a 70% phosphate removal was 200 A h m^{-3} of sewage, at a voltage of 6 V, i.e. 1.2 kWh m^{-3} . In this process the major cost is not energy since the corrosion of the graphite anode and close control needed by the process lead to heavy running expenses [11].

In the Mendia process [5], sewage with very high BOD values (≈ 1100) are treated. The fast electrolytic process (the residence time of sewage in the cell is about 10 s) removes the 65% BOD with an energy consumption of $\sim 0.5 \text{ kWh m}^{-3}$ of treated sewage. Apart from the costs, differences in the two processes mentioned are evident. In the first, the main goal is to obtain an output with a minimum fertilizer content. The aim of the second process is to obtain the destruction of all bacteria and reduce, to a large extent, the heavy polluting load of the treated sewage. Unlike the Foyn process, the Mendia process has no appreciable electrode consumption and running costs.

In our experiments, the process is not continuous and operates on waste water coming from a biological secondary treatment plant. For this reason a comparison with the energy consumption of the other processes is hardly meaningful. With regard to the removal of the phosphates (which is

mainly responsible for the eutrophication phenomenon), the smallest energy consumptions were 0.075 and 0.1 kWh m^{-3} treated sewage with a phosphorus reduction of 40 and 60%, respectively.

The results obtained in this work seem to prove that the electrolytic treatment can be considered to be an economically efficient process in removing the nutrient content of sewage. Therefore, a satisfactory resolution of the problem of tertiary water treatment with a continuous electrolytic process needs further study on cell design and electrode reactions.

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