

Treatment of Wastewaters from Manufactured Gas Plants

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The treatment of wastewaters with high concentrations of organic compounds often represents a difficult problem. In some cases, for the destruction and removal of toxic compounds using processes like biological (Alder *et al.* 1993; Morris and Lester 1994; Parker *et al.* 1994), and chemical oxidation (Beltran *et al.* 1994), were proposed. Wastewaters from manufactured gas plants contain high concentrations of organic pollutants and ammonia (Luthy 1981; Luthy *et al.* 1983). In this paper a technology for the treatment of these wastewaters is proposed. The experiments were realized with wastewaters from two Romanian manufactured gas plants. The process consists of the following steps: polycondensation–settling–stripping–biological treatment–electrocoagulation–electrochemical oxidation, or chemical oxidation.

The wastewaters were characterized by the following parameters: total organic carbon (TOC) = 5.7–16.5 g/L; inorganic carbon = 0.1 g/L; chemical oxygen demand (COD) = 67.8–84.3 g/L; phenol = 1.3–3.7 g/L; ammonia = 1.8–2.6 g/L; pH = 7.5–8.3; cyanide = 2.5–3.2 mg/L; the process was demonstrated in the laboratory and will be discussed utilizing wastewater with a content of organic compounds of 84.3 g/L. The removal of phenolic compounds by condensation with formic aldehyde was tried during the initial step. In order to determine the optimum quantity of formic aldehyde (39%) for which the removal of phenol from wastewaters is maximum, volumes of 100 mL of wastewater were treated with 0.5, 1.2, 1.5, 2.0, 3.0 mL of formic aldehyde. The samples were slowly mixed for three hours. After this time the pH of samples decreased with 1–2 units, depending on formic aldehyde quantity. Then the samples were treated with a lime solution, in order to reach a pH value of 10.5. By raising the pH, both the condensation of organic compounds from wastewater samples and the removal of the small excess of formic aldehyde was assured. After three hours from the introducing of lime, the mixing was stopped and the samples were

allowed to settle for two hours. The volume of sludge was 60–80 mL/L of wastewater, depending on formic aldehyde quantity. To establish the optimum temperature for maximum removal of organic compounds, the experiments described above were conducted at 20, 45, 60 and 90°C. The results obtained for wastewater treatment at 45 and 60°C are presented in Table 1.

The results obtained for 20°C were not encouraging, but the organic content of raw water was reduced from 16.5 g/L up to 8.75 g/L for 45°C and 8 g/L for 60°C. The increase of temperature up to 90°C did not improve significantly the removal of organic compounds. Chemical oxygen demand followed the same evolution. The residual concentrations of phenol from the samples treated at 45°C and 60°C, with 1.5 mL formic aldehyde / 100 mL wastewater, were 0.2 and 0.1 g/L. Thus, together with phenol, important quantities of organic compounds from wastewater were removed: 4.25 g/L for 45°C and 4.9 g/L for 60°C. From the results obtained it is clear that not only the phenolic compounds but also other organic compounds are involved in the condensation process. So, the appropriate name of this process is that of polycondensation. The quantity of formic aldehyde used in this process was the amount corresponding to a molar ratio of formic aldehyde:phenol of 1:3 – 1:4.

After polycondensation and settling, the ammonia concentration was 1.8 g/L. In the second step, the ammonia was removed by stripping with air, in a packed tower with the following dimensions: height = 70 cm, inside diameter = 3 cm. The pH was maintained in the range of 10.5–11.2 and the ratio of air/water was 300/1 (in L), at 25 °C; the process was conducted in counter-current. With these conditions the removal efficiency of ammonia was 95%: the residual concentration of ammonia was 90 mg/L. Ammonia was captured in a sulphuric acid solution.

Table 1. The removal efficiency of total organic carbon (TOC) and chemical oxygen demand (COD) for a wastewater by polycondensation; TOC = 16.5 g/L, COD = 84.3 g/L, phenol = 3.7 g/L

CH ₂ O volume, mL	Temperature = 45 °C				Temperature = 60 °C			
	TOC g/L	% TOC removed	COD g/L	% COD removed	TOC g/L	% TOC removed	COD g/L	% COD removed
0.5	12.5	24.2	30.2	64.2	11.5	30.3	27.2	67.7
1.2	10.7	35.1	28.6	66.1	8.75	46.9	25.3	70.0
1.5	8.75	46.9	26.8	68.2	8.0	51.5	22.5	73.3
2.0	9.25	43.9	29.6	64.9	8.5	48.5	27.5	67.4
3.0	11.7	29.1	32.0	62.0	11.0	33.3	29.6	64.8

For biological treatment a dilution of 1/5–1/6 was necessary for samples treated by polycondensation-settling and stripping. Simon's criteria for diluted wastewaters has a medium value of 0.4. After a period of acclimatization, the biodegradation of organic compounds by activated sludge process took place: chemical oxygen demand was removed from 5.0 g/L up to 1.5 g/L, and total organic carbon from 1.6 to 0.57 g/L.

In the following step, the efficiency of organic compounds separation by electrocoagulation was tested. The anode of electrolysis cell consisted of aluminium and the cathode of stainless steel. To establish the optimum current density for separation of organic compounds from wastewater, experiments were made in the range of 0.3–1 A/dm². In the wastewater from the electrolysis cell 1.2 g/L sodium chloride was introduced, and the pH was decreased to 2. The influence of electrocoagulation process on the removal of organic compounds from wastewater is presented in Table 2.

The optimum current density for the removal of organic compounds from wastewater was 0.5 A/dm², and the quantity of electricity of 0.5 Ah. In these conditions, the total organic carbon was removed from the initial value of 570 mg/L up to 305 mg/L. In the last step, the wastewater was treated by electrochemical oxidation. The results obtained for a wastewater by anodic oxidation are presented in Table 3.

Electrochemical oxidation took place in an electrolysis cell with an anode of graphite and a cathode of stainless steel. The process was discontinuous. In the wastewater sample 20 g/L sodium sulphate was introduced. The optimum working conditions were: current density = 3 A/m², quantity of electricity = 1.25 Qh. For these conditions, chemical oxygen demand was removed from 575.1 mg/L up to 150 mg/L (71%), but the content of organic carbon was not reduced in the same proportion.

In another set of experiments, after biological oxidation wastewaters were treated with sodium hypochlorite. To estab-

Table 2. The dependence of the removal efficiency of organic pollutants on quantity of electricity for a wastewater sample with total organic carbon (TOC) = 570 mg/L, chemical oxygen demand (COD) = 1580 mg/L, pH = 2, anode surface = 0.44 dm², cathode surface = 0.8 dm², J_A = 0.5 A/dm². Q = quantity of electricity (Ah), U = voltage (V).

Q Ah	U V	TOC mg/L	% TOC removed	COD mg/L	% COD removed	pH
0.1	2.6	515	9.6	1151.2	27.1	3.8
0.2	2.5	440	22.8	1018.1	35.5	4.5
0.3	2.5	370	35.0	773.4	51.0	5.9
0.4	2.5	350	38.6	632.5	59.9	6.5
0.5	2.5	305	46.4	575.1	63.6	6.5

Table 3. The evolution of a wastewater treatment by anodic oxidation; total organic carbon (TOC) = 305 mg/L, chemical oxygen demand (COD) = 570 mg/L, pH = 6.6, J_A = 3 A/dm². Q = quantity of electricity (Ah), U = voltage (V).

Q Ah	U V	TOC mg/L	% TOC removed	COD mg/L	% COD removed	pH
0.25	4.1	275	9.8	470	17.5	6.5
0.5	4.1	265	13.1	380	33.3	6.8
1.0	4.1	250	18.0	250	56.1	6.9
1.25	4.1	240	21.3	150	73.6	7.2

Table 4. The efficiency of chemical oxidation of organic compounds from a wastewater, after biological treatment.

Number of sample	Volume of NaOCl, mL	pH	TOC mg/L	% TOC removed	COD mg/L	% COD removed
0	–	6.7	570	–	1580	–
1	1	7.0	505	11.40	1141	27.78
2	2	7.0	360	36.84	842	46.71
3	3	7.0	350	38.60	580	63.29
4	4	7.0	350	38.60	342	78.35
5	5	7.1	315	44.74	338	78.61
6	8	7.0	305	46.49	171	89.18
7	10	7.1	295	48.25	112	92.91

lish the optimal conditions for chemical oxidation, the appropriate quantity of hypochlorite solution for the treatment of wastewaters was determined. Sodium hypochlorite solution had a concentration, expressed as chlorine, of 140 g chlorine/L. Wastewater samples of 100 mL were treated with different volumes of sodium hypochlorite solution: 1, 2, 3, 4, 5, 6, 10 mL, under slowly mixing conditions. The optimum value of pH for oxidation, determined by similar experiments was in the domain of 6.7 – 7.2. The results obtained for wastewater treated with sodium hypochlorite are presented in Table 4.

This wastewater had, after biological treatment, a total organic carbon content of 570 mg/L, and for chemical oxygen demand a value of 1580 mg/L. The degree of oxidation was dependent on the quantity of sodium hypochlorite: for 10 mL oxidant (12.7 g chlorine/L wastewater), chemical oxygen demand decreased from 1580 mg/L up to 112 mg/L (92.9%) and total organic carbon from 570 mg/L up to 295 mg/L (51.6%). Depending on the organic content of wastewater after biological treatment, for chemical oxidation, the necessary concentrations of chlorine was 5–13 g chlorine/L. Chemical oxidation had an efficiency close to that of electrocoagulation followed by anodic oxidation, but for great quantities of sodium hypochlorite. The results obtained for some parameters after electrocoagulation – anodic oxidation were comparable with those obtained after chemical oxidation: ammonia = 0.01– 0.03 mg/L; phenol = 0.1 – 0.3 mg/L; cyanide = 0.01 – 0.05; biochemical oxygen demand = 21 – 30 mg/L. Thus, the treatment of wastewaters from manufactured

gas plants was implemented using the following steps: polycondensation – settling – biological treatment – electrocoagulation – electrochemical or chemical oxidation, total organic carbon was removed from 16.5 g/L up to 240 – 295 mg/L, and chemical oxygen demand from 84.3 g/l up to 112 – 150 mg/L.

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