CONCEPTUAL DESIGN APPROACH FOR TREATING HIGH STRENGTH PHENOL AND FORMALIN WASTEWATER

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Abstract

Industrial effluents containing appreciable amounts of phenol and formalin may represent a problem when these effluents undergoing biological treatment. Experience in field of biological treatment for wastewater contains high concentrations of formalin showed high inhibition effect of formalin to biodegradation, specifically at higher concentrations more than 225 mg/L [3]. Also, as phenol is toxic to biological culture [7], therefore, biological culture for wastewater containing high phenol concentration, more than 250 mg/L, is just a risk.

In this paper, a problem of treating industrial wastewater contains high concentrations of both phenol and formaldehyde was encountered. As the biological treatment of such wastewater was expected to be difficult, sources of wastewater effluent were monitored, and in-site pre-chemical treatment for both phenol and formalin was designed, and experienced. With phenol and formalin being chemically oxidized and changed to either non-toxic or biodegradable constituents, entering these effluents to simple biological treatment is, therefore, found more convenient.

Keywords – industrial wastewater treatment, biodegradation, chemical oxidation, phenol, formaldehyde, BOD, COD

1. Introduction

Many industries produce wastewater that contains significant concentrations of organic constituents, measured as Biochemical Oxygen Demand (BOD) and or

Chemical Oxygen Demand (COD). The wastewaters of some industries, however, contain organic compounds that are included in the priority pollutants such as phenol and formaldehyde. These organics are incompatible with the processing at municipal wastewater treatment facilities, and not effectively treated by municipal wastewater treatment plants, and usually cause significant problems. Pre-treatment is therefore found essential to deal primarily with constituents that are incompatible with municipal sewage treatment.

Studies on biodegradation of wastewater containing formaldehyde showed the inhibition effect of formaldehyde on degradation [3]. A method to convert formaldehyde to an easily biodegradable substance is here-in used. Sodium sulphite is found to react with formaldehyde forming sodium formaldehyde bisulphite [8], which is not only non-toxic to microorganisms but also, a biodegradable substance.

Also, phenol shows an inhibitory effect to biochemical reactions, specifically at high concentrations. Chemical oxidation process is also used here to transform phenol to less objectional intermediates. This process involves contacting wastewater containing phenol with an oxidizing agent (hydrogen peroxide) for the oxidation of phenol to carbon dioxide and water in the presence of ferrous iron catalyst and at a reaction pH of 4.0 [7].

2. Materials and methods

Mansoura for Resins & Chemical Industries Co. was constructed at 1963 for the production of resins and other chemical synthesis. Figure (1) illustrates general layout for the company. These industries utilize phenol and formaldehyde as a key chemical inorganic synthesis including synthetic resins and other products. Wastewaters from these industries usually contain high concentrations of phenol and formaldehyde.

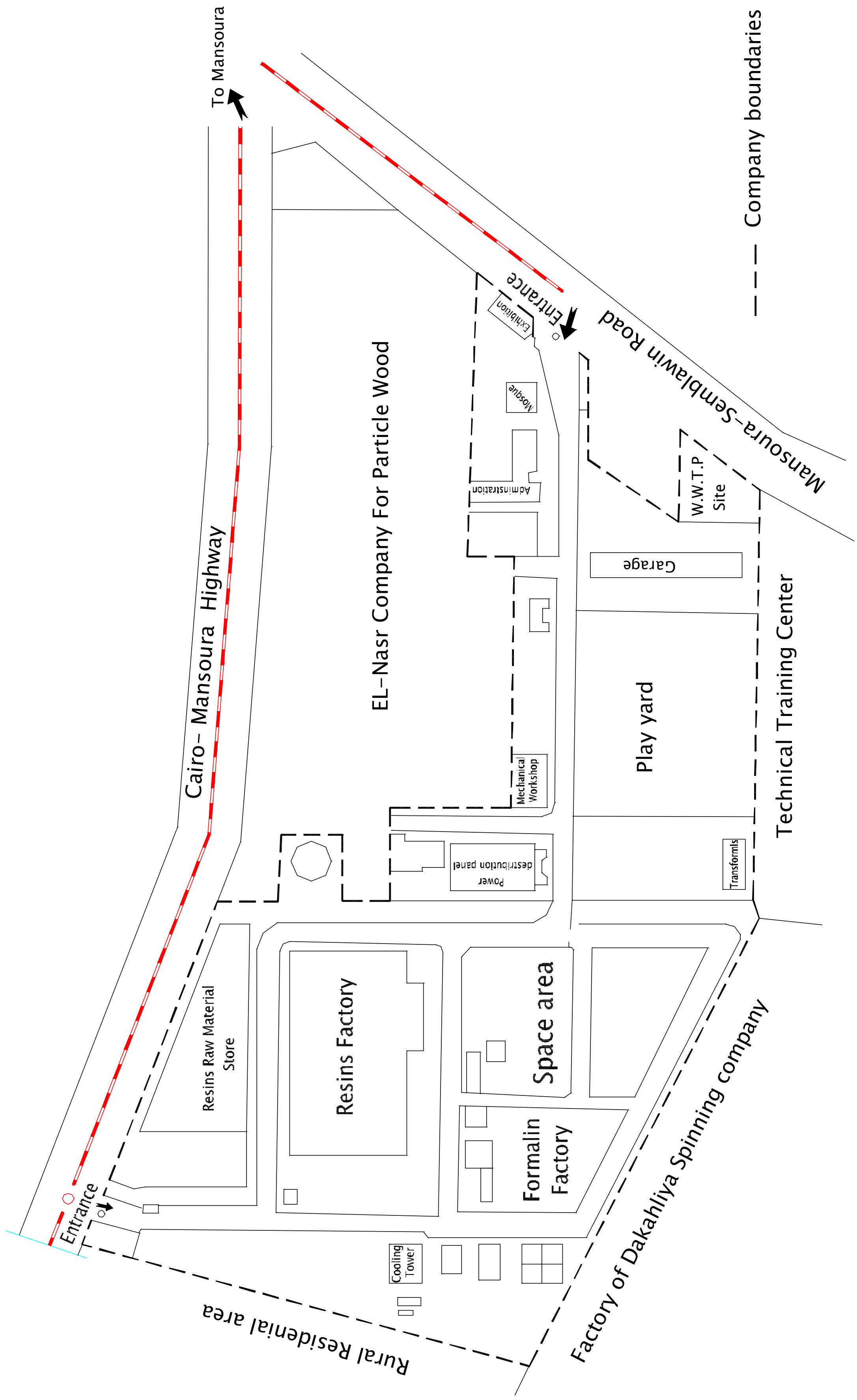


Figure 1. General layout for Mansoura for Resins &Chemical Industries Company

2.1. Field studies

Flow measurements:

One of the main objectives of the study was to firmly measure the flow rates of the produced wastewater at the factories aiming at determining the wastewater discharge from different sources.

Sampling and analysis

Wastewater samples were collected in February-March 2002. Sampling 20 litre vessels were used for collection of composite samples for determining the main relevant characteristics. Moreover, the wastewater analyses for each stream were performed over a reasonable time to accurately determine the characteristics in terms of pollutant concentration.

Figure (2) illustrates a sewer map for the investigated industrial activity where the sampling points are located. Also, table (1) represents the daily flows measured at these sources of wastewater and average recorded wastewater characteristics at these sources.

All the analyses were carried out according to the methods outlined in the Standard Method for the Examination of Water and Wastewater Analysis (APHA, 1985). BOD was measured using BSB-controller model 1020 T, WTW, W.G., (constant temperature respirometer). COD was measured using dichromate method. Suspended Solids was measured using the conventional method and pH was measured using pH meter, Cole-Parmer, U.S.A.

Phenol was determined using brominating mixture method [10] with a slight modification in order to make it capable for detecting phenol even at lower concentrations (standard 0.5mg/1 phenol solution was accurately detected) [3].

Formalin was determined quantitatively by using the iodometric method [10].

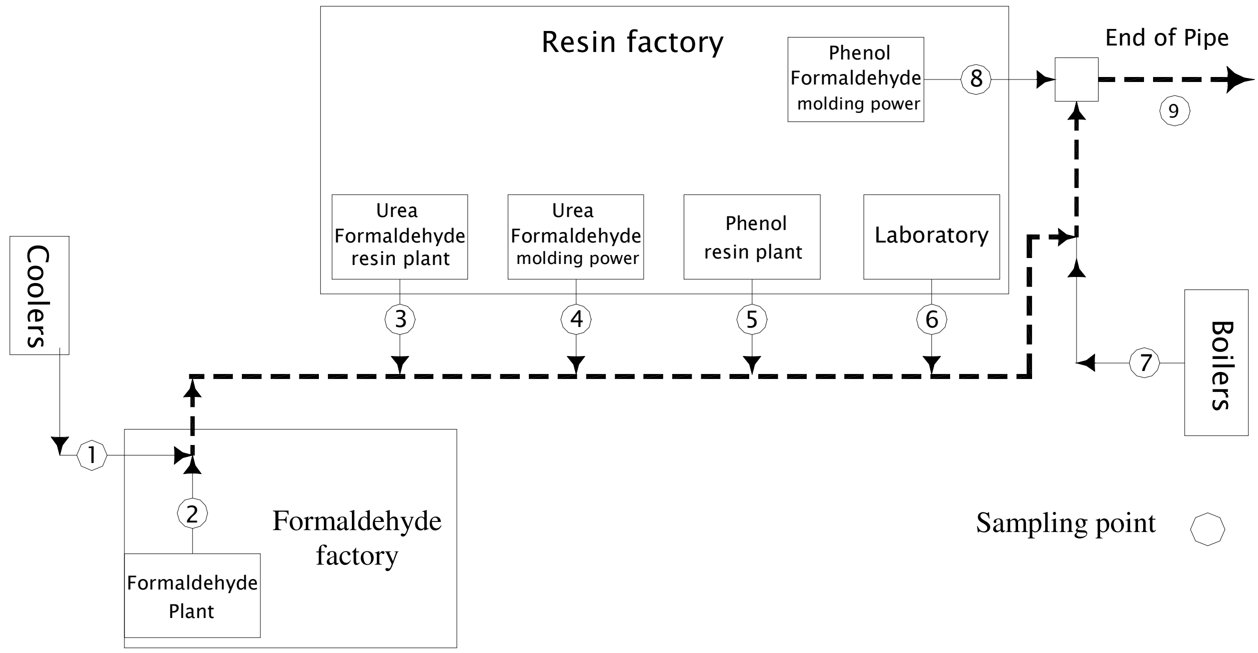


Figure 2. Sewer map for the investigated industrial activity

Table (1). Average flows and wastewater characteristics recorded at different sources of wastewater

Source	Coolers	Formaldehyde plant	Urea Formaldehyde Resin Plant	Urea Formaldehyde Molding Powder	Phenol Resin plant	Laboratory	Boilers	Phenol Formaldehye Molding Powder	End of Pipe
Sampling point	**1**	**2**	**3**	4	**5**	**6**	**7**	**8**	**9**
Average flow m^3/d	**293**	**45**	**40.6**	**38.4**	**76**	**52.8**	**19.2**	**1.35**	**566**
p H	**7.98**	**8.61**	**8.0**	**8.2**	**8.4**	**9.15**	**10.1**	**8.5**	**8.3**
Temp. °c	**34.4**	**27.1**	**37**	**28**	**36**	**32.6**	**55.6**	**30**	**31**
Conductivity µ.mohs	**1702**	**586**	**2183**	**1787**	**2098**	**2305**	**2132**	**2011**	**1799**
TSS mg/l	**31**	**51**	**94**	**24.8**	**30.2**	**43**	**1474**	**101**	**157**
COD mg/l	**10296**	**3629**	**7920**	**2947**	**19800**	**643**	**653**	**4676**	**4652**
BOD_5 mg/l	**7920**	**2490**	*	**1783**	*	**563**	**542**	**2499**	**2024**
Phenol mg/l	**164**	**179**	**130**	**105**	**2308**	**25**	**120**	**113**	**675**
Formaldehyde mg/l	**198**	**251**	**6360**	**255**	**195**	**34**	**142**	**190**	**1752**
N (TKN)mg/l	**212**	**221**	**448**	**216**	**618**	**43**	**32**	**636**	**513**

*BOD_5 cannot be accurately determined due to high strength of phenol & formaldehyde.

2.2. Pretreatment studies

Pre-chemical treatment (oxidation) is widely used as pretreatment step before biological treatment. Chemical oxidation, in general, is appropriate for the following circumstances:

- Concentrated waste streams with relatively low flow,

- Wastewater with constituents that inhibit or upset biological treatment in wastewater treatment plant,
- Wastewater that contains highly reactive compounds.

In selecting a chemical oxidation pretreatment process, typically desirable and sometimes competing factors are:

- Economic feasibility, including minimal capital and operating costs,
- Reactions that will not produce undesirable secondary pollutants (for example, chlorinated organics),
- Treatment effectiveness relative to quantity of oxidizing agent used,
- Integration of the oxidation process into an existing or proposed treatment system, and
- Few site-specific constraints (such as space).

2.2.1 Chemical oxidation (pretreatment) of phenol

This process involves contacting wastewater with an oxidizing agent (hydrogen peroxide) under certain conditions such as pH of 4.0 with presence of catalyst ($FeSO_4$) to obtain the desired reaction [2,7]. The following is a typical oxidation reaction showing hydrogen peroxide oxidation of phenol to corbon dioxide and water in the presence of ferrous iron catalyst and at a reaction pH of 4.0.

$$C_6H_5OH + 14H_2O_2 \longrightarrow 6\,CO_2 + 17H_2O \qquad (1)$$

Chemical oxidation has been applied to the pretreatment of phenol from industrial wastewater. However, oxidation reaction is not specific and other constituents in the wastewater are expected to be oxidized. Figure (3) illustrates a chemical oxidation system, typically adopted, consists of mixing the wastewater and hydrogen peroxide, storage and feed systems for oxidant and catalyst, pH control facilities, and other systems for control of flow and chemical dosages.

Chemical oxidation is greatly affected by conditions such as pH, temperature, contaminant concentration, contact time, and the presence of other oxidant-consuming constituents in the wastewater.

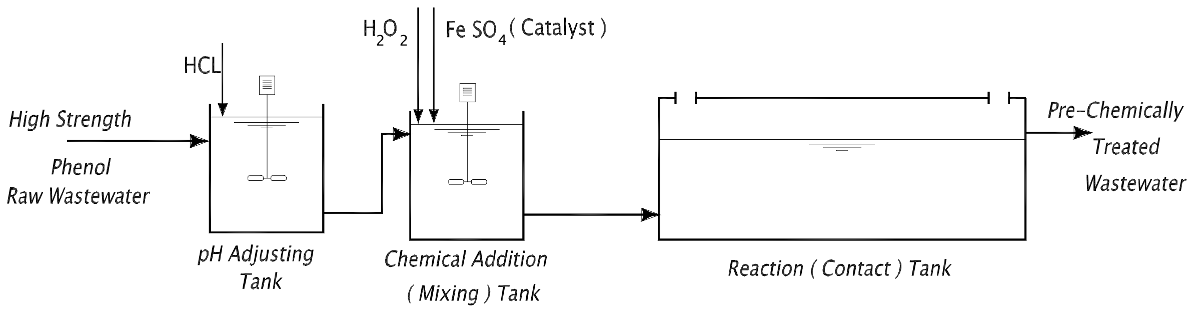


Figure 3. Schematic flow diagram for In-site phenol pre-chemical oxidation unit

2.2.2 Chemical oxidation (pretreatment) of formaldehyde

In case of effluents containing formaldehyde, the biological treatment alone is just a big risk [3]. Addition of sodium sulphite to the wastewater containing formaldehyde in the presence of water, sodium formaldehyde bisulphite is obtained according to the following equation [8].

$$CH_2O+Na_2SO_3+H_2O \longrightarrow HOCH_2.NaSO_3+NaOH \qquad (2)$$

Sodium formaldehyde bisulphite is not only non-toxic to microorganisms but also a biodegradable substance. Figure (4) illustrates a chemical oxidation system, typically adopted, consists of mixing the wastewater and Na_2SO_3, with storage and feed systems for Sodium sulphite and other systems for control of flow and chemical dosages.

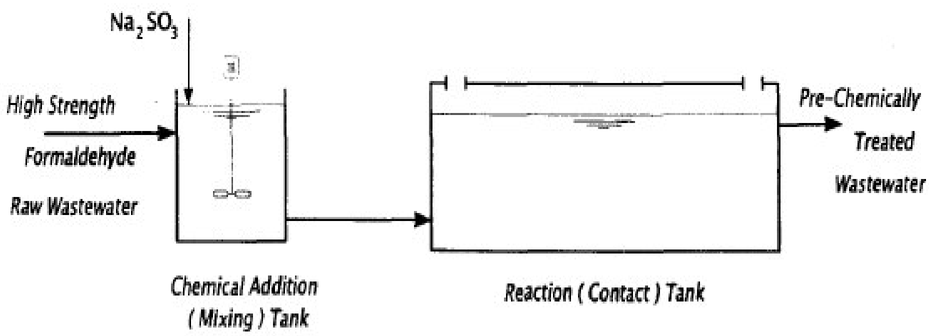


Figure 4. Schematic flow diagram for In-site formaldehyde pre-chemical oxidation unit

3. Results and Discussion

Characteristics of different sources of wastewater, as pre-stated in Table (1), illustrate high strength of formaldehyde from urea formaldehyde resin plant at point No. 3, also, high strength of phenol from phenol resin plant at point No. 5. Samples of the different sources were checked from biodegradation view point. In biodegradation experiments of wastewater containing formaldehyde, results showed high inhition effect of formalin, which increased with increase of formaldehyde concentration. Previous studies [3] stated that of a wastewater samples containing formaldehyde ranging from 225 to 315 mg/L, residual formalin ranging from 40% to 80%, respectively, was found at the end of the run (12-16d). The biodegradation of formalin decreased significantly at concentrations higher than 300 mg/L.

Investigation also proved biodegradation of phenol after relatively long time, usually took 9-12 day for about 80% removal of phenol which initial concentration ranging from 150-210 mg/L. Previous studies [3], also, stated that with the same phenol concentration but with increased concentration of microorganisms, phenol removal was faster indicating that phenol biodegradability is to some extent dependent on microorganism concentration. Yet, biodegradation of phenol still needs relatively long time which found uneconomic and technically not accepted.

Investigation on formaldehyde pre-treatment

Characteristics of the industrial effluents, as illustrated in Table (1) for each source of wastewater, indicate a wide range of wastewater characteristics specifically concerning formaldehyde in the wastewater from urea formaldehyde resin plant. The collected samples were checked for biodegradability, with the results obtained showed very high inhibitor effect of formaldehyde to biodegradation. For these samples, a process of formaldehyde pre-chemical oxidation was conducted.

Waste flow from urea formaldehyde resin plant ranged about 40.6 m^3/d. Treatment of formaldehyde (CH_2O) in this smaller amount of flow is considered technically wise.

The process involved the addition of sodium sulphite to wastewater containing formaldehyde, in the presence of water, this results in forming sodium formaldehyde bisulphite which is not toxic to microorganisms and also biodegradable. Table (2) illustrates average results obtained through analysis of formaldehyde oxidation using sodium sulphite.

Table (2). Average results obtained through analysis of formaldehyde oxidation using sodium sulphite.

Formaldehyde concentration mg/L	6360*	3360	330	46	36	26	21
Formaldehyde percent removal %	—	47	94.8	99.2	99.4	99.6	99.67
Dose of Na_2SO_3 gm/L	—	0.25	0.5	0.55	0.6	1.0	1.25

* initial concentration - PH = 7.8 - Reaction time ≃ 30-40 min.

Investigation on phenol pre-treatment

Pre-chemical oxidation (pre-treatment) was conducted to the high concentration of phenol existed in the raw wastewater effluent from phenol resin plant at source No. (5). The main objective of this investigation was to confine the problem of phenol at its source (origin), thus, avoiding inhibition effect of phenol on the biological activity when biological treatment is conducted to the end of pipe of the whole factory effluent.

Waste flow from phenol resin plant ranged about 76.0m^3/day. A treatment of phenol (C_6H_5OH) in this relatively small amount of wastewater by $H_2O_2/FeSO_4$, which is called “Fenton’s reagent” [9], makes sense. A pH of 4.0 was found to be optimum.

The industrial effluent previously illustrated in table (1), showed wide range of characteristics, specifically concerning phenol in the wastewater from phenol resin plant. The collected samples were checked for biodegradability. The results obtained showed inhibition of phenol to biodegradation. For these samples, pre-chemical treatment for phenol oxidation was carried out. The processes of oxidation involved, in its first step, contacting the raw wastewater with hydrochloric acid for lowering the pH down to 4.0.

The second step is the addition of metal, $FeSO_4$ solution, that have special oxygen transfer properties which improve the utility of hydrogen peroxide, results in the generation of highly reactive hydroxyl radicals (OH). Table (3) illustrates average results obtained through analysis of chemical oxidation of phenol using H_2O_2 with the presence of $FeSO_4$. However, it should be mentioned that H_2O_2 is expected to oxidize to certain limit some of the other pollutants in the wastewater, specifically formalin.

Table (3). Average results obtained through analysis of phenol oxidation using iron-catalyzed hydrogen peroxide

Phenol concentration mg/L	2308*	1400	716	37	18	14	9.5
Phenol percent removal %	—	40	69	98	99.2	99.4	99.6
Dose of H_2O_2 gm/L	—	8.5	16.5	21.5	23.0	25	30

*initial concentration Dose of $FeSO_4$= 90mg/L Reaction time ≅ 30-60 min.
- Initial pH = 8.8 Adapted reaction pH=4.0

Biological (secondary) treatment

After the pre-chemical oxidation for these effluents containing high strength of either phenol or formalin, the whole effluents is collected through a newly constructed sewerage network through the factories area. The whole effluent wastewater is directed to biological treatment unit designed according to criteria adopted through experiments as follows;

- Average daily discharge $Q_{av} = 566\ m^3d^{-1}$

- Average wastewater characteristics was determined after pre-chemical treatment, for formaldehyde from urea formaldehyde resin plant, and for phenol from phenol resin plant, by preparing a mixture of wastes from these sources after pre-treatment, with the other sources, previously illustrated in Figure (2), with the same ratios of their daily discharges. Table (4) illustrates the average wastewater characteristics for mixtures obtained after pre-treatment.

Table (4). Average wastewater characteristics after pre-treatment

Parameter	pH	TSS mg/L	COD mg/L	BOD_5 mg/L	Phenol mg/L	Formaldehyde mg/L	Total N mg/L
Concentration	6.5	165	4150	2685	125	167	458

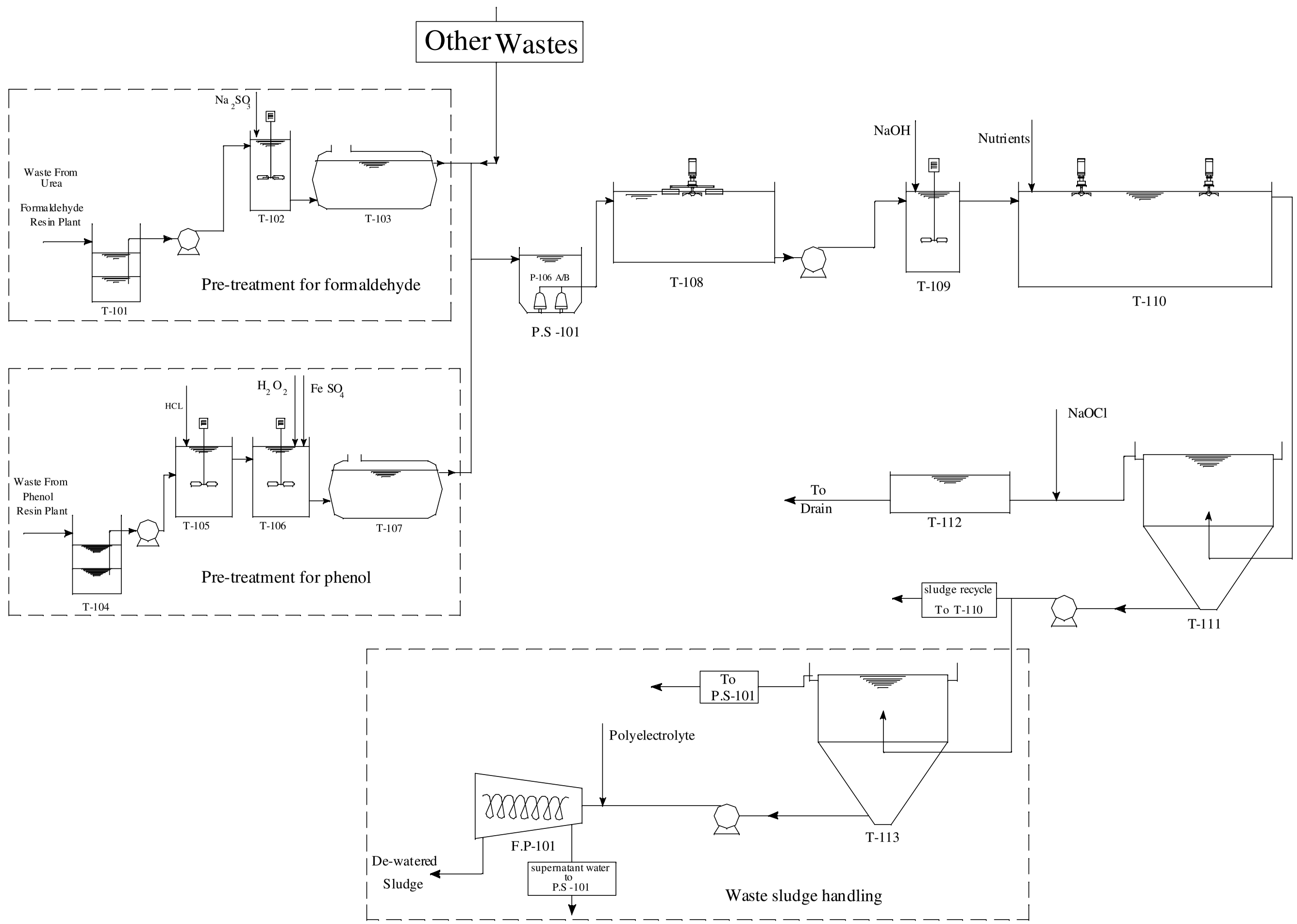
Figure (5) illustrates flow diagram for the treatment system adopted for Mansoura for Resins and Chemical Industries Company. However, this system depends mainly on the simple and effective idea of primarily treating the sources with high strength either toxic or non-biodegradable pollutants at its origins. In this case pre-chemical oxidation for phenol and formaldehyde is applied as follows;

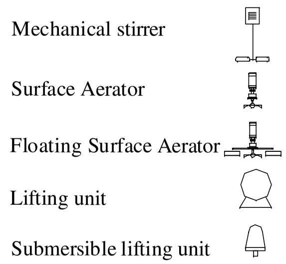
Formaldehyde pre-chemical treatment at its point source:

- Addition of Na_2SO_3 to the raw wastewater in a mixing tank of about 30 sec. retention time.
- Entering the mixture to a contact tank of 40 min. retention time to allow the reaction to overcome.

Phenol pre-chemical treatment at its point source:

- Adjusting pH at 4.0 as required for reaction conditions.
- Addition of H_2O_2 in the presence of iron catalyst Fe SO_4, in a mixing tank of 30 sec. retention time
- Entering the mixture to a contact tank of retention time 60 min., in order to allow reaction to take place.





Tag.No	Description	Qty.	Size/Capacity
T-101	Receiving Tank from Urea Formaldehyde Plant	1	2.0 m^3
T-102	Na_2SO_3 Mixing Tank	1	1.0 m^3
T-103	Formaldehyde Pre-treatment Tanks	2	1.5 m^3 Each
T-104	Receiving Tank from Phenol Resin Plant	1	2.0 m^3
T-105	pH Adjustment Tank	1	1.0 m^3
T-106	(H_2O_2+ Catalyst) Mixing Tank	1	1.0 m^3
T-107	Phenol Pre-treatment Tanks	2	2.0 m^3 Each
T-108	Equalization Tank	1	6.0x6.0x4.0 m depth + 0.5 m FB
T-109	pH Adjustingt Tank	1	2.0 m^3
T-110	Aeration Tank	1	9.0x18.0 x4.0 m depth + 0.5 m FB
T-111	Secondary Clarifier Tank	1	7.0x7.0x3.5 m depth + 0.5 m FB + 3.0 m Hopper
T-112	Contact Tank	1	2.0x4.0x1.5 m depth + 0.5 m FB
T-113	Sludge Thickener	1	3.0 m diax 3.5 m water depth + 3.0 m Hopper
P.S-101	Collecting Pump Station	1	2.0x2.0x3.5 m depth
F . B-101	Sludge Filter Press	1	1 m^3 \hr

Figure 5 . schematic flow diagram for the wastewater treatment system adopted for Mansoura for Resins and Chemical Industries Company

As illustrated in Figure (5), the biological treatment, in addition to the accessories including pump station of the raw wastewater and other pumping units, mainly consists of the following constituents;

- **Equalization tank**

144.0 m^3 volume, and about 6 hrs retention time. This tank is mainly used to accommodate flow variation at different sources, and to maintain to certain limit, an average flow characteristics.

- **pH adjusting tank**

60 sec. retention time with stirrer and its all other accessories including NaOH tanks and dosing pumps.

- **Aeration tank**

648 m^3 volume, and retention time of 28 hrs. It should be mentioned that experiments indicated that no need for using primary sedimentation, before entering the biological treatment, due to the low efficiency of the primary sedimentation.

- **Final sedimentation tank**

49 m^2 surface area, operated with surface loading rate of 14 $m.d^{-1}$.

- **Sludge recycle pumps**

These pumps are used to withdraw activated sludge from the final sedimentation and recycle it to the aeration tank, with the excess waste sludge being disposed to sludge treatment.

- **Contact tank**

12.0 m^3 volume, and 30 min. retention time for disinfection of the treated effluent from the final sedimentation using sodium hypochlorite.

- **Waste sludge handling**

Waste sludge is being treated through two stages;

First stage

- Sludge thickening using gravity thickener of 3.0 m diameter. The supernatant wastewater is recycled to biological treatment while the thickened sludge is directed to a filter press.

Second stage

- The thickened sludge is directed to sludge filter press.

Note: Drying beds is also recommended for sludge treatment, yet the problem encountered is the shortage of area required, and to some extent, the nature of drying beds.

4. Conclusions

Due to the high inhibition effect of phenol and formalin to biodegradation, therefore, for biological treatment of wastes containing either phenol or formaldehyde, it was found essentially to apply in-site pre-treatment for these constituents at their sources, before being collected with other wastes and before entering biological treatment.

A treatment of phenol in smaller amount of wastewater, that contains high strength phenol, makes sense. Iron-catalysted hydrogen peroxide was found effective in phenol oxidation. An initial pH of 4.0 is required, then, after 30-60 min. the reaction is completed in open vessel, with final pH of about 2.5.

For formaldehyde, addition of calculated amount of sodium sulphite to the wastewater reacts with formaldehyde forming sodium formaldehyde bisulphite, after about 40 min., which is not only non-toxic to microorganisms but also a biodegrable substance; this allowed the microbial biodegradation to take place without inhibition when entering biological treatment.

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