Effluent Wastewater Treatment for a Resin-Based Paints Plant (Case Study)

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This work is concerned with the treatment of wastewater obtained from the resins plants, which is the basic constituent for paints industry. Inspection of the existing units and evaluation of its performance have been done .The analysis of wastewater effluent from tanks during washing process and treatability study for wastewater have been conducted. The experiments have been done on the pinch scale unit to determine the optimum dose of the coagulant added to the wastewater for primary treatment. The used coagulants in this study are aluminum sulfate (Alum) $[AI_2(SO_4)_3.18H_2O]$, and anionic polyelectrolyte. The impact of the dose on outlet water characteristics such as pH, turbidity, total suspended solids and chemical oxygen demand were determined for monitoring the treating system./This work concludes the suggestion of the necessary solutions according to the results of treatability study, designing of three configurations schemes to treat the wastewater, conducting cost/benefit analysis for the proposed alternative schemes and selection of the preferred treatment scheme. The wastewater treatment plant was implemented and operated efficiently according to the selected preferred integrated. scheme using sequential batch reactor as a biological treatment system

Keywords:

Wastewater, Resins, Air flotation, Paints, Biological treatment.

Introduction:

Resin factory is one of the plants that belong to El-Obour Pakin For Paints And Chemical Industries. The company is located in the industrial zone of El-Obour city, Cairo and it is surrounded by industrial area. The factory, which is built over a total area of about 100 acres, works 200 days/year; three shifts/day the resin plant produces 18,000 tons/year of resin.

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Existing Situation And Environmental Problems: Synthetic resins prepared from materials having no resin properties. There are many types of resins such as:

Alkyd resins: They are commonly used in paints and varnishes. They are prepared by condensing dicarboxylic acids with polyhydric alcohols.

Urethanes resins: They are strongly adherent to metal and resist both chemical attack and abrasion. The advantages of using synthetic resins are that they have great resistance to weather conditions and chemicals.

Description of production plant: El-Obour Pakin Co. consists of the following main production plants; water-based paints plant (WBP), solvent-based paints plant (SBP), resins plant (RP).The procedures of resins production are summarized as follows :

Raw materials are fed to the Jacketed stainless steel chemical reactor provided with mixer (there are three tanks with 10,000 lit capacity and three tanks with 6,000 lit capacity).

The mixer may be similar to a large dough kneader with sigma blades. As a result of chemical reaction and high temperature, vapors of xylene are evolved with water vapor contaminates. The xylene-water vapor mixture is condensed in shell and tube condenser where water is used as a cooling media as shown in Fig. (1).

The condensed xylene-water mixture is fed to a gravity separator to separate liquid xylene. Xylene is recycled to the reactor while water, which is loaded by small amount or xylene is treated in a special incinerator where gas oil is used as a fucL After complete reaction, the product is withdrawn from the reactor to a thinning tank to cool the product and to separate any impurities during production process.

The product is then discharged to a storage tanks via adjusting tanks. The cooling water is recirculated through cooling towers. Only make- up water is added in the cooling tower to overcome losses resulting from windage, evaporation and blowdown, After the production of resins, washing water and caustic soda are used to clean the chemical reactor before charging it.

Caustic soda solution (2% cone.) is used as a cleaning medium, where the temperature of reactor is increased to 90 °C using steam passing in the jacket. After washing period $(1.5 - 2.0 \text{ hrs})$, the contents of the reactor are withdrawn as a wastewater as shown in

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Fig. (1). The main raw materials in resin plant are shown in table (1). While the list of products are shown in table (2)

Description of water and wastewater:

Water usage: Water is used in the resin factory for cleaning and make up for cooling system. The consumption rate for make up is 6 $m³/hr$ while the consumption rate for cleaning and washing the batch reactors is about 20 m³/day (2.0 m³/hr)

Raw materials	Consumption rate, ton/year		
Phthlaic anhydride	1,800		
Glycerol	700		
Xylene	500		
Vegetable oils	4,500		
Pentaerythritol	600		
Dryers	20		

Table (1) List of main raw materials

Wastewater distribution: The wastewater effluent from gravity separator is heated and treated in a special incinerator while the wastewater resulting from washing and cleaning the reactors must be treated to comply with Environmental Law no. 93/1962 modified by decree 44/2000 for discharging into public sewer system.

Wastewater characteristics: Composite samples were carried out in this search for the effluent of resin factory. Table (3) shows the results of these analyses. The results show that the plant violates the law in pH, COD, BOD and Oil & Grease.

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Remedial Measures Schemes

In order to achieve the project activities, alternative schemes based on the results of the .treaiability study conducted on the sample of wastewater are developed and weighted against each other from which a preferred integrated configuration is finally selected based on both technical and financial basis.

Treatability study{l>

Scope of the work: This section deals with the developmeni of economical and environmentally acceptable technology for wastewater treatment discharged from the resin factory. Firstly, it is conducted to obtain a full image of the processing step is inside the factory. Based on these results, a composite sample has been collected and analyzed quantitatively and qualitatively.

Based on this type of industry, the following parameters were used to make the assessment: pH, Total suspended solids. *Chemical* oxygen demand, Biological oxygen demand, TKN, Oil and grease, Total phosphorous and Total solids at 105 °C.

Following the assessment, a series of bench-scale experiments have been conducted to define the best way and the optimum operating conditions for the treatment process to be implemented on a full scale. Selected coagulants for the chemical treatment have been chosen. These coagulants were Aluminium sulfate and two poly-anionic electrolytes. Design parameters have been determined and alternatives for wastewaler treatment are presented in the following;

The wastewater contains high concentrations of organic matter represented by chemical oxygen demand, which represents here about 5100 mg O₂/L exceeding the standard, which is 1100 mg COD/L. Two thirds of the chemical oxygen demand is present in soluble form providing 2770 mg $O₂/L$ as shown in table (3).

The wastewater also contains high values of BOD, TKN, and phosphorous levels. These values are exceeding the standard values for wastewater to achieve the requirements of Law 93/1962 and its amendment No 44/2000 to ensure the compliance of the factory effluent with the quality standards for discharge into the sewer.

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Parameters	pН	$\mathsf{T}.{\tt COD}[\text{\tt S}.{\tt COD}]$		BOD	TKN	TSS	T.P.	Oil and grease
Unit	\sim \sim				mgO_2/l mgO_2/l mgO_2/l mgN_2/l mg/l		mpP/I	mg/l
Value	11.5	5100	2770	3060	113	706	18	156
Legal Values by Law	$6 - 9.5$	1100		600	100	800	25	100

Table (3) Raw wastewater characteristics *

* T.COD (Total COD), S.COD (Soluble COD), TKN (Total Kejldhal Nitrogen) and T,P (Total Phosphorous)

Jar test and key design parameters⁽²⁾: It can be concluded that two thirds of wastewater is in soluble form and other part is in colloidal matter which could be removed by using an appropriate coagulant without addition of calcium oxide or any alkali (because the pH value is in the alkaline range).

To define these key design parameters, a series of jar tests using aluminum sulfate and two poly-anionic electrolytes at different doses were conducted. We took into consideration the pH, turbidity, total suspended solids and chemical oxygen demand as monitoring parameters to compare between them and deflne which one is the best and most economically effective for evaluation.

Methodology

(a) Using aluminum sulfate (A/am): The solution of the Alum has been prepared at concentration of 50 mg per each ml of the solution. Flash mixing *is* started at *180* RPM and continued for two minutes during which the Alum has been added at concentrations of 0, 100, 200, 300, 400 and 500 mg/l. pH of the jars has been adjusted at 9 using sulfuric acid. Following the flash mixing a flocculation for 15 minutes is done after which sedimentation for 30 minutes is carried out, then the samples have been withdrawn using siphon and analysis is then proceeded as shown in table (4)

(b) Using poly-anionic electrolyte; The same procedure has been conducted for the two poly-anionic electrolytes like Alum. The two polymers are prepared at concentration of 1 mg / ml of the solution using distilled water. Two sets of jar test have been conducted; one set for each polymer. The concentrations of the polymers were 0, 4, 8, 12, 16 and 20 mg/l. At the end of each test, the samples were collected and analyzed for pH, turbidity, TSS and COD as shown in table (5).

Results and discussion:

-Treatment using aluminum sulfate (Alum; Referring to table (4), the measured parameters are pH, turbidity, TSS and COD. The sludge that has been accumulated forms scum layer on the top of the wastewater. Fig. (2) shows the turbidity, TSS and COD concentration for effluent wastewater after treatment with alum.

-Treatment using poly-anionic electrolyte: Referring to table (5) and figures (3&4)), it can be concluded that, the two polymers are not efficient for the removal of the soluble COD matter and it increases the value of the COD over that of the raw wastewater so it is not suitable for use. Referring to table (5), the optimum dose of alum is 400 mg/1, which is providing good results (providing effluent with 2400 mg COD/I and 10 mg/1 TSS). According to previous results, dissolved air flotation technology is the best way for preliminary treatment of such type of wastes after coagulation / flocculation stage using

Table (4) Treatments with Alum.

Alum with 400-mg/l dose. The treated effluent from dissolved air flotation must be biologically treated to comply with the Environmental Law.

Alternative Integrated Treatment Schemes⁽³⁴⁴⁾:

Three alternatives configurations are developed as remedial measures. The proposed alternatives consist of physical-chemical treatment, biological treatment and sludge dewatering system. We can use parts of the existing treatment unit for water -based paints to

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treat the resin plant waste stream, therefore it is very important to describe the technology adopted in the water-based paints wastewater treatment plant.

Item	Dose, mg/l	TSS, mg/l		Turbidity		COD mg/l		pH value	
		Po.1	Po.2	Po.1	Po.2	Po.1	Po.2	Po.I	Po.2
Raw	$\bf{0}$	706	706	348	348	5100	5100	11.5	11.5
T1	4	35	16	66	50	6300	3270	11.6	12.3
T ₂	8	26	22	56	57	6390	3510	11.9	12.3
T ₃	12	55	25	73	57	7230	4500	12.1	12.4
T ₄	16	58	33	74	59	7320	4920	12.1	12.4
T5	20	32	42	57	66	7350	7830	12.2	12.4

Table (5) Treatments with polymers

Description of treatment train for wat<mark>er-based paints wastewater stream (30 m³/d)⁽⁵⁾</mark> The raw wastewater leaving water-based paints plant is fed to an equalization tank via manual screen as shown in Fig. (5). The effluent from the balancing tank is fed to the mixing tank where Ca $(OH)_2$, Na₂CO₃ are added to decrease TDS concentration and adjusting pH of solution. After that the waste stream is fed to a sedimentation tank via coagulation and flocculation stage with Alum & polymer. In the primary sedimentation tank, suspended solids are separated. The clarified stream is then fed to aeration tanks (Two aeration tanks with diffused air system) where O_2 added to reduce BOD and COD. The treated effluent from biological tanks is subjected to settle in a secondary sedimentation tank where sludge is separated and part of it is returned to the ueration tank for regeneration.

The treated effluent from biological tanks is further disinfected by sodium hypochlorite solution and then filtered through sand filter. The treated effluent is discharged to the public sewer system and sludge formed in sedimentation tanks and biological tanks are fed to the sludge thickening tank and then to the filter press where solid content in the sludge is about 30-40%.

Fig.(3) **Effect of polymer (1) dose on oultlet water characteristics**

Fig.(4) Effect of polymer (2) dose on outlet water characteristics

Alternative treatment scheme # (I): In this alternative, raw wastewater $(2 \text{ m}^3/\text{hr} \text{ max.})$ capacity) is allowed to pass through manual bar screen to separate any suspended solids with particle diameter ≥ 15 mm. The effluent stream from screen flows by gravity to an aerated equalization tank (about 16 m³ volume) provided with a suitable mixing device to make concentration of pollutants homogeneous in the wastewater. The equalized stream is then pumped by a suitable pump to physical /chemical treatment unit (dissolved air flotation) where the influent is coagulated before entering DAF unit by Alum as a suitable coagulant. The treated effluent from DAF unit is then fed to a biological treatment unit (sequential batch reactor or bio- filter or fixed media reactor) after it had been equalized through an aerated equalization tank as shown in Fig. (6). The treated effluent is discharged to public sewer system while sludge formed in a biological reactor, reaction tank and dissolved air flotation unit is thickened and dewatered in the sludge tank and in the filter press of the existing treatment unit for water- based paints wastewater. Table (6) shows the design parameters for this unit and also the expected parameters after treatment.

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Parameter	Design value	Expected value		
Q	20 m^3 /d	--		
COD	Min.: 5,100	< 1000		
	Max: 25,900			
	Avg.: 15,000			
BOD	Min.: 3,060	$<$ 500		
	Max: 15,600			
	Avg.: 8,000			
TSS	Min.: 700	< 700		
	Max: 8,500			
	Avg.: 5,000			
Oil & grease	160	< 50		
pH	$13 - 14$	$6 - 9$		

Table (6) design influent and expected effluent parameters

Alternative treatment scheme # (2): In this alternative, raw wastewater (2 m³/hr max. capacity) is allowed to pass through manual bar screen, aerated equalization tank (about 16 m³ volume) and DAF unit like the previous alternative.

The treated effluent from DAF unit is then fed to aeration tanks (two tanks with 70 $m³$ volume each). The aeration tank is provided with aeration system and oxygen measuring device and control system for each tank. The effluent from aeration tank is fed to a settling tank to separate formed sludge. Part of the sludge is returned to aeration tank. The treated effluent from settling tank is discharged to public sewer system while sludge resulted in settling tank, reaction tank and dissolved air flotation unit is thickened and dewatered in the sludge tank and in the filter press of the existing treatment unit for water -based paints effluent.

The design parameters for this unit and also the expected parameters after treatment are the same for alternative $# 1$. Fig. (7) shows the block diagram for this treatment scheme.

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Alternative treatment scheme # (3): This alternative depends on conducting of continuous system based on aeration tank with clarifier for integrated waste of resin plant and water based plant. In this alternative, raw wastewater $(2 \text{ m}^3/\text{hr} \text{ max. capacity})$ is allowed to pass through manual bar screen to separate any suspended solids with particle diameter \geq 15 mm. The effluent stream from screen flows by gravity to an aerated equalization tank (about 16 m³ volume) provided with a suitable mixing device to make homogenous concentration of pollutants in the wastewater. The equalized stream is then pumped by a suitable pump to physical /chemical treatment unit (dissolved air flotation) where the influent is coagulated before entering DAF unit by Alum as a suitable coagulant.

The treated effluent from DAF is mixed with physically and chemically treated stream, resulting from water -based paints plant (30 m³/d) as shown in Fig.(8). The mixed stream (50 m^3 /d) is then equalized in the aerated equalization tank where the influent characteristics are shown in table (7).

From previous results, the BOD load will be doubled due to mainly the increase in hydraulic load therefore the equalized stream is fed to aeration tanks (two tanks existing and two tanks will be conducted $(2*35m^3$ each)) as shown in Fig. (8).

The aeration tank will be provided with aeration system and oxygen measuring devices and control system for each tank. The effluents from aeration tank are fed to a settling tank to separate formed sludge.

Part of the sludge is returned to aeration tanks. The treated effluent from settling tank is discharged lo public sewer system while sludge resulted in settling tank, reaction tank and dissolved air flotation unit is thickened and dewatered in the sludge tank and in the filter press of the existing treatment unit for water- based paints effluent.

Cost Estimation^{$(6,7&8)$}:

The economic comparison for the proposed alternatives is based on the following criteria:

i- *Fixed capital investment;* Manufacturing fixed capital investment represents the capital necessary for the installed process equipments with all auxiliaries that are needed for complete process operation such as: equalization tanks, reaction tank, sequential batch reactors, pumps, aerators, compressor and dissolved air flotation unit, expenses for piping required from resin reactors to WWTP, instrumentation for pH, temperature and $O₂$ content, foundations and civil work for aeration tanks,

Fig. (7) Block diagram for alternative scheme # **2**

2- *Operating and maintenance cost:* Direct operating cost includes expenses directly associated with the manufacturing operation (treatment of wastewater). This cost involves chemicals required for treatment (coagulant, flocculent and acid cost), direct operating labor; supervisory and clerical labor directly connected with the treatment unit; plant maintenance and repairs; and electrical power.

Table (8) shows the comparison between proposed alternatives from fixed capital investment and operating & maintenance cost point of view,

Justification For The Preferred Integrated Scheme $^{(2)}$:

Technical and economical comparison of the proposed alternatives including cost benefit analysis has been conducted for each of the three alternatives for the remedial measures. Based on both technical and economical comparison of these alternatives against each other, alternative (1) is selected as the preferred integrated scheme (PIS).

Technical justification for PIS

The alternative (1) is technically superior with respect to other alternatives due to the following reasons:

Table (7) Influent and expected effluent parameters

Item			Alternative Alternative Alternative		
	Description	(1)	(2)	(3)	
	Fixed capital investment, EGP				
	a) Installed equipment cost $+$ instrumentation $+$ piping $+$ pumps + control	600×10^{3}	670×10^{3}	720×10^{3}	
	b) Civil work	70×10^3	120×10^{3}	100×10^{3}	
	c) Piping from resin plant to WWTP (stainless steel, 252 m)	52×10^{3}	52×10^3	52×10^{3}	
	Total Cost	722×10^{3}	842×10^{3}	872×10^{3}	
$\mathbf{2}$	Annual operating and maintenance cost, EGP	100×10^{3}	120×10^{3}	125×10^{3}	

Table (S) Economic comparison between alternatives

(l) General consideration: Alternative (1) is specially suited for resin plants in case of shut down of water -based paint plant or changes in pollutant concentrations. These situations do not affect the efficiency of the integrated WWTP.

(ii) Biological treatment^{$(2x3)$} The advantages of sequential batch reactor (SBR), biofilters and fixed media reactor are the easy and simple operation, easy removal of sludge and short retention time compared with aeration tanks.

In addition, the aeration process in each unit previously -stated is better than aeration mechanism in aeration tanks. Moreover the control of air velocity, pressure and flow rate is easier than in aeration tanks. Volume of SBR, rotary filter and fixed -media reactor is smaller than aeration tanks, which require larger area, and the aeration tanks in the WWTP for water -based paints plant is not working efficiently where the activated sludge biological treatment technique is not used (no microorganisms are present).

Economical justification for PIS

The proposed alternatives are compared financially against each other. The criteria used for comparison are: Fixed capital investment and annual operating & maintenance cost The alternative (i) is financially preferred due to minimum fixed capital investment and annual operating & maintenance cost as shown in table (8).

Conclusions and recommendations

This work has been directed towards the selection of the best way for wastewater treatment of resin tanks washing water. The study involved bench-scale investigations to determine the type and optimum dose of coagulant used in preliminary treatment to reduce the loads of suspended solids and hence the organic load from wastewuter stream. Alum and two types of polymers are used as coagulants and flocculants. Results revealed the following:

- The DAF technology is the best way for preliminary treatment such type of wastes after coagulation / flocculation stage using Alum with 400-mg^l dose. The treated effluent from dissolved air flotation must be biologically treated to comply with Environmental Law No. 93/1962 modified by decree 44/2000
- Three alternatives configurations were suggested as remedial measures. The proposed alternatives consist of physical-chemical treatment, biological treatment and sludge dewatering system.
- Technical and economical comparison for the proposed alternatives including cost benefit analysis was conducted for each of the three alternatives for the remedial measures.
- Alternative (1) is selected as the preferred integrated scheme based on both technical and economical comparison of these alternatives against each other.
- The wastewater treatment plant was installed and operated efficiently according to the selected preferred integrated scheme using sequential batch reactor as a biological treatment system

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