B. Antizar-Ladislao
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Editors

Water Resource Planning, Development and Management

Water Production and Wastewater Treatment

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WATER RESOURCE PLANNING, DEVELOPMENT AND MANAGEMENT

WATER PRODUCTION AND WASTEWATER TREATMENT

B. ANTIZAR-LADISLAO
AND
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PREFACE

This book includes selected paper and is the result of a very successful 3-day symposium on *Water Production and Wastewater Treatment – Technologies, Advances and Issues* as part of the *8th World Congress of Chemical Engineering* in Montreal in August 2009 which my colleague, Dr. Blanca Antizar-Ladislao, and I organized and convened.

The importance of the topic showed the interest, almost 100 paper and poster presentations, and number of people participated and contributed to the symposium. There were excellent talks covering various aspects and topical issues related to water production and wastewater treatment in industrial and municipal sectors.

Some talks were focused on removal of a specific contaminant, specific technology for the process, experimental findings, or process modeling. Others had wider perspective and were covering the importance of water production and wastewater treatment in the context of our current industrial society and the energy and climate change. The papers covered a unique mix of issues related to both water production and wastewater treatment.

Success of such events always depends on many people and factors. I would like to gratefully acknowledge the financial contributions of Royal Academy of Engineering for travel and attendance at the Congress. I would also like to thank all the participants and presenters at the Symposium for their contribution enriching the Symposium, my colleagues at the technical committee and reviewers for assisting in selection and review of papers, and Dr. Antizar-Ladislao for her significant contributions in co-organizing the Symposium with me.

Professor Roya Sheikholeslami, Ph.D., P.Eng., C.Eng., F.I.ChemE
Chair of the Organizing Committee
Symposium on Water Production and Waste Water Treatment
8th World Congress of Chemical Engineering

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Chapter 1

TREATMENT AND REUSE OF WASTEWATER FROM A PETROCHEMICAL COMPLEX

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ABSTRACT

Wastewater from petrochemical complexes is characterized by a diversity of pollutants, including free and emulsified hydrocarbons, phenols, cresols, xylenols, sulfides, ammonia and cyanides. The treatment of this wastewater is usually based on a multiple stage approach, consisting of physical, chemical and biological treatment processes. Wastewater treatment and reuse has been developed and applied at a petrochemical complex in Haifa, Israel. The solution was based on: (a) multiple stage treatment, creating several technological barriers, in order to avoid uncontrolled emissions into the neighboring marine environment; (b) maximal reuse of treated effluent and oil, for minimizing the disposal of pollutants outside the industrial zone; (c) step-by-step development, design and implementation of the treatment process enabled to establish the best operation and efficiency at the existing units and these could be used as starting conditions in the development of the next treatment stages; (d) flexibility and complete independent operation of the treatment units significantly increased the reliability of achieving a final effluent of high quality. The biological treatment process has been efficiently protected by preliminary flow regulation, to control hydraulic and pollutant loading. Additional protection of the biotreatment was achieved by the removal of free and emulsified oil by gravitational oily-water separators (API) followed by dissolved nitrogen flotation (DGF). Biotreatment is achieved by aerated ponds followed by a submerged biological contactor (SBC) for the removal of dissolved organics and for nitrification. Effluent polishing treatment is operated by chemically-enhanced sedimentation and by sand filtration. The treatment-recycle system in the petrochemical industry provides cost-effective solutions and high quality effluent to the recipient water

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bodies. The approach of treatment-recycling serves as a trigger to the industrial management, in addition to regulatory requirements, to invest in water treatment facilities.

INTRODUCTION

Process and manufacturing plants usually consume large amounts of water in various operations of production, cleaning and rinsing. Wastewater contains pollutants that are frequently environmentally regulated. An effective way to minimize wastewater and pollutant emissions is to design wastewater recycling, so that the used water could be reused to a maximum extent in the same plant.

Petrochemical complexes are producing large amounts of wastewater, which is characterized by a diversity of pollutants including free and emulsified hydrocarbons, phenol, cresols, xylenols, sulfides, ammonia, and cyanides. The production processes usually include distillation, catalytic cracking, visebreaking, oil and waxes, ethylene, sulfur recovery and other processes. Due to national or regional water shortage, which results in low fresh water consumption, as well as the variety of production processes, petrochemical wastewater in arid or semi-arid regions are characterized by high concentrations of pollutants. They include several periodical streams from gasoline, kerosene and other products washeries, containing up to 12 percent phenols, most of them cresols and xylenols.

Diwan et al. (1995) mentioned a great potential for recycling of effluents to solve water shortage for the industries, since in many cases the cost of treatment is modest compared to overall benefits. Asano et al. (1996) mentioned the status of national policies on wastewater treatment, wastewater reuse characteristics and some wastewater reuse experiences in Japan. Au et al. (1996) reported a great economic efficiency obtained by the use of a low cost filtration system working on petrochemical secondary effluent.

Wijesinghe et al. (1996) reported a study based on the use of secondary effluent as cooling water makeup for inland industry in Australia. Brown and Mountain (1998) reported findings regarding general feasibility of wastewater reuse as cooling tower makeup at power plants in Maryland, USA. Buhrmann et al. (1999) used a spiral reverse osmosis plant to treat mine water and spent cooling water producing a new source of water for a power station.

Angelakes et al. (1999) presented the status of wastewater reclamation and reuse around the Mediterranean basin and discussed existing guidelines and regulations, also presenting the possibility of developing uniform wastewater reuse standards. The potential for the recovery and reuse of cooling water in Taiwan has been reported by Shu-Hai et al. (1999). A brief overview of the reuse of treated industrial wastewater in cooling water systems is provided by Phulwar et al. (1999), including a case study of the reuse of treated effluent as cooling water at a refinery process plant in India. Large wastewater reuse projects in the UK, based on long-term international operation experience on reuse projects for the petrochemical, power and paper industries are discussed by Durham (2000). Yang et al. (2000) introduced a mathematical approach to design an optimal network when multiple pollutants are contained and the treated effluent can be reused to a maximum extent in the same plant.

Zhong and Lai (2009) reported the reuse of effluent from a petrochemical company for make up to the cooling system. Wong (2000) described the pilot testing and implementation of a major advanced wastewater reclamation project to recover secondary effluent from a municipal plant and blowdown from a cooling tower for reuse in a large petroleum plant. Durham (2000) reported about large wastewater reuse projects in the UK based on long term international operation experience on reuse projects for the petrochemical, power and paper industries. In the field of wastewater treatment processes membrane technology, especially membrane bioreactor (MBR) is being applied (Llop et al., 2009, Fratila-Apachitei et al., 2001, Galil et al., 2009).

This chapter deals with a research and development project, which was carried out at a petrochemical complex located at a distance of about two miles from the Mediterranean coast in the Gulf of Haifa, Israel. The program included characterization of the wastewater main stream, as well as lateral streams generated by specific production processes (Galil et al., 1988). Laboratory and pilot plant studies on flocculation-dissolved air flotation (Galil and Wolf, 2000) enabled the design and operation of a full-scale treatment plant. A comparative study of three alternative biological processes: activated sludge, rotating biological contactor and aerated ponds provided the data for a biological treatment process based on two aerated lagoons in series, accomplished by a lime softening-clarification chemical plant (Galil and Rebhun, 1990; Galil and Rebun, 1991). A survey of the biological process occurring in the recirculated cooling system of the industrial complex enabled to operate this system as the recipient of the treated effluent, as well as a polishing nitrification bioreactor (Rebhun and Engel, 1988).

Following the research results and conclusions, the full scale developed solution for treatment and reuse of petrochemical wastewater was based on: (a) multiple stage treatment, achieved by combining physical, chemical and biological processes, creating several technological barriers in order to avoid uncontrolled emissions into the neighboring river and marine environment; (b) maximal recycling of treated effluent and oil, for minimizing disposal of pollutants outside the industrial zone (Galil and Rebhun, 1992).

BASIC CONCEPTS

The implementation of environmental quality regulations, regarding the disposal of effluent to the environment, usually to water bodies, is imposing careful considerations. By lowering the level of pollutants to the values required by the regulations, the treated effluent and some of the constituents separated from the wastewater could be considered for recycling by the petrochemical complex. This would minimize the disposal outside the industrial zone.

In the case of the Haifa petrochemical complex, the research and development project included the following tasks: (a) characterization of the main raw wastewater streams, as well as lateral streams generated by specific production processes; (b) feasibility studies of general treatment of all the wastewater streams versus separate treatment of concentrated streams; the investigated process was based on chemical emulsion-breaking, flocculation and dissolved air flotation (DAF); (c) a comparative study of three alternative biological treatment processes for the removal of dissolved organic matter; (d) a survey of the processes occurring in the water cooling system of the complex, including studies on the use of treated effluent as makeup; (e) characterization of two different types of sludge produced by the wastewater treatment and development of sludge treatment methods.

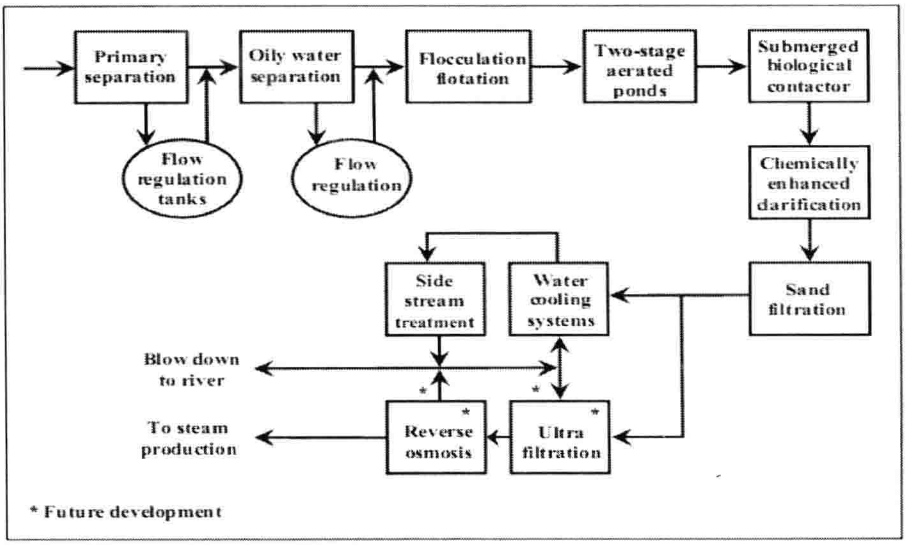

Figure 1. General description of the wastewater treatment-reuse system.

Following the conclusions of the research and development project, the wastewater facilities of the Haifa petrochemical complex include: separate storage and treatment of the concentrated phenol (spent soda) streams; storage and flow regulation (equalization) of the main raw wastewater stream; gravitational oil-water separator (OWS); chemical flocculation and dissolved gas (nitrogen) flotation (DGF); biological treatment for carbonaceous substrate removal; biological treatment by submerged bio-contactors (SBC) for nitrification; chemical precipitation for softening and clarification; sand filtration; effluent reuse as makeup in the water cooling system; blow-down treatment by chemical precipitation-sedimentation before the final disposal to the river; sludge collection, treatment and disposal. A general description of the wastewater treatment-reuse system is described in Figure 1.

DESCRIPTION OF TREATMENT UNITS

Flow Regulation: The main wastewater stream could be influenced by factors such as rain floods and spills caused by unexpected accidents at the production units. For minimizing these influences, two flow regulation tanks with a total capacity of 45,000 m3 were built and connected to the system. The operation of these tanks, having a capacity of about five days of maximal flow, enables the operators to avoid sudden hydraulic or pollutant surges on the treatment units.

Concentrated wastewater streams: Studies carried out by Galil and Rebhun (1988) indicated severe disturbances and inhibition caused by phenols included in the spent soda streams coming from the gasoline and other product washeries. As part of the general project, the concentrated spent-soda wastewater streams were separated from the sewerage system, stored in special tanks and gradually treated. The treatment is based on neutralization and separation between: gases, which are conducted to the flare; an oily phase including the phenols is recycled to the production processes; a water phase containing mainly inorganic salts is drained to wastewater.

Chemical flocculation and flotation (DGF): Laboratory and pilot plant studies have been carried out, developing design and operational parameters for this process. The flotation unit is covered in order to avoid VOC's emissions, therefore nitrogen is used instead of air. The flotation systems consist on three parallel units with a capacity of 200 m3/hr each. The flocculant in use is a cationic polyelectrolyte in a dose of 7 to 10 mg/L. Later studies performed by Galil and Wolf (2000) on this wastewater indicated that the chemical flocculation - DGF could remove efficiently the emulsified phase, which could be aggregated and separated up to the surface. However, it was found that the process could also remove substantial amounts of dissolved organic matter, due to the hydrophobic characteristics of some of the substances, which could bind to the solid surfaces.

Biological treatment: A comparative study has been carried out including activated sludge, rotating biological contactor (RBC) and aerated lagoons (Galil and Rebhun, 1990). These bioprocesses represent different concepts: activated sludge and RBC are considered as intensive processes, developing high concentrations of active biomass and high cell residence time (CRT), while aerated ponds are considered as a partial bioprocess, involving low biomass and low CRT values without biosolids recycling. The aerated ponds alternative was adopted because of the possibility of lowering the investment cost. It was clear that in this case, additional biotreatment would be necessary. This alternative was based on sharing the bioprocess tasks between: (a) the aerated ponds, performing carbonaceous substrate removal (two days detention time); (b) second stage biological treatment by submerged biological contactors (SBC), mainly for nitrification; The experience accumulated over the last ten years shows that this combination has achieved good and reliable biological treatment (Table 1).

Chemical clarification: A chemical contact flocculation-clarification unit, designed for a flow of 600 m^3/hr is operated for efficient separation of biosolids and clarification. A second identical unit works on the treatment of water from inside the cooling system (side stream treatment). Part of the side stream treated effluent goes back to the cooling system, while the remaining effluent is disposed off to the neighboring river (Figure 1). Both contact flocculation-clarification units are operated at pH values of 10.7 by addition of lime for enabling removals of calcium carbonate and magnesium hydroxide. The removal of suspended solids is being enhanced by the use of a cationic polyelectrolyte as aid coagulant.

Filtration: A gravity sand filtration unit operates after chemical enhancement by a cationic polyelectrolyte. The effluent fits all the quality requirements for being reused as make up in the cooling system or for being discharged to the river. In the future the filtration effluent will be treated by ultra filtration, reverse osmosis and reused as make up to steam production for the local power station (Figure 1).

Sludge treatment: The petrochemical complex wastewater treatment system is producing two categories of sludge: (a) oily sludge is produced by oily water separators, by the dissolved gas flotation and also includes sediments from crude oil storage tanks. The oily sludge is gravitationally thickened in long term concrete storage tanks, chemically conditioned and cake-filtered by geo-tubes. The oil is recycled to production and the water phase is returned to wastewater treatment. (b) sludge produced by the biological treatment stages (biosolids) is obtained from the chemical clarification and from the backwash of the sand filters. This sludge is stabilized by land farming and transported to landfill sites. In the future all sources of sludge will be treated by cake filtration and by thermal technologies (Figure 2) for maximizing recyclable materials and improve land utilization.

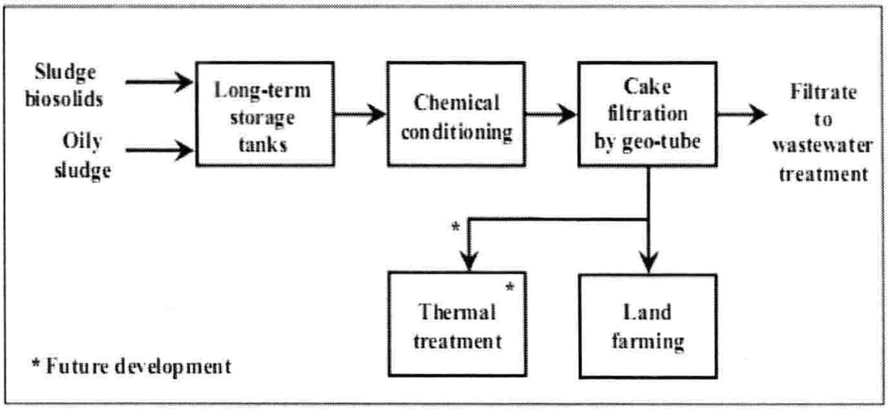

Figure 2. General description of the sludge treatment system.

EFFLUENT QUALITY

Table 1 presents the results obtained as part of a six years (2003 to 2008) monitoring of the last wastewater treatment stages, which are DGF, aerated ponds, submerged biological contactor and chemical clarification followed by sand filtration. The results are expressed in statistical terms which include 50% and 80% probabilities of obtaining values equal to or less than the stated magnitudes. Table 1 also indicates average values and standard deviation. The parameters reported include pH, total organic carbon, total suspended solids, oil, ammonia nitrogen, nitrate nitrogen and phosphates.

Table 1. Effluent quality after different treatment stages

Statistical Parameter	pH	TOC (mg/L)	TSS (mg/L)	OIL (mg/L)	NH_4-N (mg/L)	NO_3-N (mg/L)	PO_4 (mg/L)
DGF EFFLUENT							
50%	7.6	59		16	9.5	0.9	2.0
80%	7.8	81		25	14.0	2.5	2.8
Average	7.6	53		23	10.9	1.7	2.0
St. Dev.	0.3	27		14	8.7	2.8	0.9
AERATED PONDS EFFLUENT							
50%	7.8	28	45	7.4	6.3	0.8	0.7
80%	8.0	43	68	13.7	9.5	2.7	1.4
Average	7.9	33	51	11.4	6.8	2.5	1.0
St. Dev.	2.6	17	27	18.4	4.9	4.7	1.8
SUBMERGED BIOCONTACTOR EFFLUENT							
50%	8.0	14	37	4.1	0.1	32.2	1.3
80%	8.1	19	56	7.6	0.2	42.0	2.0
Average	7.9	17	42	6.4	0.5	32.9	1.5
St. Dev.	0.2	11	24	11.8	2.0	14.7	0.9
SAND FILTRATION EFFLUENT							
50%	8.1	5.7	5.6	1.8	0.1	28.7	0.6
80%	8.2	7.9	8.2	3.4	0.2	37.1	0.8
Average	7.9	6.8	6.4	2.3	0.4	31.7	0.7
St. Dev.	0.2	3.2	3.8	0.8	0.7	15.8	0.4

The final effluent, after sand filtration, contains less than 10 mg/L of TOC, less than 10 mg/L of suspended solids, less than 1 mg/L of ammonia nitrogen and less than 1 mg/L phosphates. This effluent is being reused as make up to the water cooling systems as well as for fire fighting. In the future part of the effluent will be additionally treated and reused for steam production (Figure 1).

CONCLUSIONS

The project involves several technological barriers for protecting river and sea water and for enabling sustainable effluent reuse:

- hydraulic barrier is achieved by the storage-flow regulation tanks;
- physical and chemical barriers include four different treatment stages of gravity separation, chemically enhanced flotation, chemical clarification and sand filtration before reuse or final disposal;
- biological barriers include two separate processes: aerated ponds and submerged biological contactors.

Flexibility, as well as complete independent operation of the treatment units, significantly increased the reliability of producing a final effluent of high and reliable quality. The recycling of oil and sludge has minimized the disposal of contaminants outside the industrial zone.

The treatment-recycle system in the reported petrochemical industry provides cost-effective solutions. The reuse of treated effluent at the Haifa petrochemical complex saves about 2.5 million cubic meters of fresh water per year, which is the equivalent water consumption of a town with a population of 45,000. The cost of this amount of water, if purchased from the national resources would be close to one million US dollars per year.

The cost-effective approach of treatment-recycling serves as a trigger to industrial management, in addition to the regulatory requirements, to invest in water treatment facilities.

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