CHEMICAL ENGINEERING TRANSACTIONS

VOL. 88, 2021

A publication of AIDIC

The Italian Association of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Petar S. Varbanov, Yee Van Fan, Jiří J. Klemeš

ISBN 978-88-95608-86-0; **ISSN** 2283-9216

DOI: 10.3303/CET2188082

Efficient Design and Sustainability Assessment of Wastewater Treatment Networks using the P-graph Approach: A Tannery Waste Case Study

Emmanuel A. Aboagye[a], Jean Pimentel[b], Ákos Orosz[c], Heriberto Cabezas[d], Ferenc Friedler[e], Kirti M. Yenkie[a,*]

[a] Department of Chemical Engineering, Henry M. Rowan College of Engineering, Rowan University, Glassboro, NJ, USA
[b] Department of Chemical and Environmental Process Engineering, Budapest University of Technology and Economics, HU
[c] Department of Computer Science and Systems Technology, University of Pannonia, Veszprém, Hungary (HU)
[d] Research Institute of Applied Earth Sciences, University of Miskolc, Miskolc, Hungary
[e] Széchenyi István University, Győr, Hungary.
yenkie@rowan.edu

In the tannery industry approximately, 30 - 35 m^3 of wastewater (WW) is generated per ton of rawhide processed. The WW comprises high concentrations of salts, ammonia, dye, solvents, and chromium. Of particular interest is chromium, which has been proven to cause dermatological, developmental, and reproductive issues on exposure. Thus, there is a need for appropriate treatment of the tannery WW before it is discharged for natural remediation. However, designing a treatment process is multifaceted due to the availability of multiple technologies that can perform similar tasks and the complex composition of waste streams. This necessitates the treatment to be performed in stages namely, primary, secondary, and tertiary. In some cases, pretreatment is required to enhance the recovery in the following stages. Due to the combinatorial nature of this problem, the P-graph approach, which uses principles from graph theory, can be used to synthesize a treatment pathway by selecting appropriate technologies at each stage, while meeting required purity specifications. Furthermore, the P-graph approach can provide alternate feasible treatment structures ranked based on Economics as well as Sustainability indicators, such as the Sustainable Process Index (SPI). In this work, a tannery WW case study is investigated with multiple stages and treatment technologies. A complex maximal structure is generated comprising all possible technologies, flows, connections, bypasses, mixers, and splitters. The models for each technology involve capital and operating costs, efficiency, and SPI at each stage of the treatment process. This problem is formulated in P-graph and solved using the Accelerated Branch-and-Bound algorithm.

1. Introduction

The growth in population and industrialization has increased the demand for water (McDonald et al., 2011). Thus, securing an adequate water supply is vital for sustaining anthropogenic activities and improving the sustainability of the ecosystem (Kundzewicz, 2007). The increasing problem of water availability can be mitigated via the treatment of wastewater (WW) for reuse. However, according to the 2017 report on water development by the United Nations Educational, Scientific and Cultural Organization (UNESCO, 2017) over 80% of all WW is discharged without treatment globally. Therefore, there is a need to develop efficient treatment processes to recover the untapped resource in the form of WW.

1.1 Wastewater Treatment (WWT) synthesis: A systems engineering problem

Treatment of WW is one of the essential steps in reducing aqueous pollution and improving the quality of the ecosystem (Metcalf and Eddy, 2002). However, WWT is a complex process influenced by several factors such as physical, chemical, and biological (Aboagye et al., 2021). In addition, the amount of waste accumulation, composition, and treatment technology selection plays an important role during WWT synthesis (Yenkie, 2019). This complexity is associated with the different sources of WW. Depending on the source, the waste composition

Paper Received: 10 June 2021; Revised: 19 August 2021; Accepted: 9 October 2021
Please cite this article as: Aboagye E.A., Pimentel J., Orosz Á., Cabezas H., Friedler F., Yenkie K.M., 2021, Efficient Design and Sustainability Assessment of Wastewater Treatment Networks using the P-graph Approach: A Tannery Waste Case Study, Chemical Engineering Transactions, 88, 493-498 DOI:10.3303/CET2188082

is dominated by specific contaminants (Gadipelly et al., 2014). As such, the synthesis of WWTNs should not be performed independently based on a single body of knowledge but should be an integrated approach via a systems engineering methodology (Crini and Lichtfouse, 2018). The systems engineering approach expands and recognizes that complex processes comprise interrelated factors. Hence, its application leads to improved criteria for designing sustainable WW treatment processes. Therefore, the generation of WWTNs should consider several areas such as ecology, economics, engineering, environmental science, sustainability, and biology to appreciate their interdependencies.

1.2 Case study on Tannery Industry: magnitude and impacts of tannery wastewater

The tannery industry is one of the major sources of WW. In 2016, about 30,000,000 tons of rawhide were processed in the United States (US) (Tribe, 2016). Since 30 – 35 m^3 of WW is generated per ton of rawhide processed (Saxena and Bharagava, 2016), it can be estimated that about 900,000,000– 1,050,000,000 m^3 of tannery WW is generated in the US annually. The different chemicals used in the processing of the rawhide into leather contribute to a diverse range of pollutants and in turn the difficulty associated with the treatment of tannery WW. The tanning process is the primary cause of chromium, ammonium, and chloride salts in the WW, while the beamhouse contributes the highest organic and sulfide contents (Saxena and Bharagava, 2016). Tannery WW is a major reason for health and environmental concerns if not treated properly before discharge due to the higher concentrations of organics, sulfides, suspended solids, and chromium (Elsheikh, 2009). The presence of chromium, which is known to cause several dermatological, reproductive, carcinogenic, and developmental effects (Shrivastava et al., 2002), makes WW treatment originating from tannery industries a crucial problem that needs immediate attention (Chowdhury et al., 2015). Thus, the Tannery WW case study is investigated using the P-graph approach in this work. A complex maximal structure is generated comprising all possible WW treatment technologies, flows, connections, bypasses, mixers, and splitters. The models for each technology involve capital and operating costs, efficiency, and SPI at each stage of the treatment. Details of the problem formulation and results are presented in sections #2 and #3.

2. Methodology

2.1 Stagewise design of WWT networks

Traditionally, a wastewater treatment plant (WWTP) can be partitioned into preliminary, primary, secondary, and tertiary treatments, or stages, according to the type of operations involved. Preliminary treatment is employed to remove total solids and large objects that reduce the performance of subsequent systems. In primary treatment, physical operations are used to withdraw settleable and floating materials. In secondary treatment, operations based on biological or chemical principles are used to remove chemicals and most of the organic matter. Tertiary treatment is employed in cases where some pollutants cannot be removed by previous stages, or to eliminate harmful constituents, such as endocrine disruptors. Each stage of WWT can comprise more than one operating unit; thus, it may be regarded as an individual structure for separation during process design. Systematic synthesis of these stages requires the algorithmic definition of the superstructure problem. In this work, the methodology proposed by Yenkie et al. (2021) is employed to determine the set of candidate units and their plausible connectivity. The principles of operation, and typical efficiencies of contaminants removal, are considered to identify the plausible sequences of operations and alternative connections for each stage. Hence, a comprehensive structure can be obtained when the desired removal is not achieved via one technology. The superstructure of the entire process is constructed stagewise by replicating the structure of the n-th stage for each feasible outlet stream of the previous stage.

2.2 The P-graph approach

The P-graph approach is a graph-theoretic framework for the systematic design of processes (Friedler et al., 1992); the framework is based on a set of axioms and algorithms as well as on a bipartite graphical representation of process units that enables the combinatorial handling of a design problem. When employing the P-graph approach, the problem is depicted as a set of materials represented by circles (M-type nodes) and a set of operating units represented by horizontal bars (O-type nodes). The P-graph algorithms generate a rigorous superstructure, or maximal structure, from the set of operating units and materials in the initial problem's definition (Friedler et al., 1993). Such generation is guided by the P-graph axioms, which exclude any structural inconsistencies of the model and avoid incomplete structures that misguide the optimization. This constitutes an advantage when compared to traditional superstructure-based optimization methods, as errors are prevented and every operation included is useful for at least one solution, which avoids unnecessary complexity. Moreover, the algorithms exploit the structural properties of the network to handle the binary terms and accelerate the solution of the optimization. This is achieved by reducing the size of the problem and enhancing the bounding step. Additionally, the methodology renders the set of n-best designs derived from the operations pre-defined by the designer. In traditional approaches the ranked set of solutions is not readily available (Yenkie et al.,2019), and commonly requires the introduction of further constrains and modification of the initial model, thereby requiring additional time and computational efforts.

2.3 Tannery WW case study

Contaminants were grouped into five main categories to simplify the problem. TSS comprised total suspended solids. The metal contaminants typically included heavy metals, namely Mn^{2+}, Zn^{2+}, As^{3+}, Pb^{2+}, Cd^{2+}, Ni^{2+}, Co^{2+}, and Fe^{2+}. Though chromium(VI) (Cr^{6+}) can be categorized as heavy metal, it was separated from that category as it is a major pollutant of concern in the tannery industry due to the recalcitrant nature of its removal. The chemical contaminants consisted mainly of anions, namely SO_4^{2-}, PO^{4-}, NO^{3-}, and Cl^-. The pollutant with the least permissible limit was used as the outlet specification for each category of contaminant. Table 1 shows the inlet and outlet contaminant concentrations. The assumed entering flow rate of WW was 100 m^3/h.

Table 1: Table for case study inlet and outlet specifications

Contaminant	Inlet concentration (mg/L)	Outlet specification (mg/L)
TSS	258	≤100
Metal	250.20	≤0.1
BOD/COD	5,958.62	≤30
Chromium	23.07	≤0.01
Chemical	3,459.32	≤30

2.4 Structural complexity

Table 2 presents the candidate operating units for each stage. The initial structure of the case study is generated by carrying out the systematic stagewise synthesis procedure listed in Yenkie et al. (2021). This also includes the ability to bypass a stage, when not required. Upon deployment of the P-graph approach, the number of plausible outlet streams found for stages 1, 2, and 3 are 4, 39, and 10, respectively. Thus, 1720 operating units are employed to model the feasible paths for treatment, whereas 1720 auxiliary units are used to represent the mixing operation. Furthermore, 3447 M-type nodes are deployed to depict the materials of the structure. The optimization problem encompasses 3447 inequalities for the balance of materials and 3440 continuous variables that represent the size of the units. Additionally, an equivalent number of binary variables is considered to represent the inclusion or exclusion of the units in the structure. Although the number of binary variables increases exponentially the difficulty of the problem, these variables are effectively handled employing the combinatorial algorithms of the P-graph framework. In this work, it is assumed that the cost of the operating units are fixed-charge linear functions that depend on the flow rates of streams entering the operation. Additionally, mixing operation is considered only in the final stage before the final product, which preserves the linearity of our overall model.

Table 2: Operating units for each stage

Stage 1 operating units	Stage 2 operating units	Stage 3 operating unit
Sedimentation (Sdm)	Rotating biological contactor (Rbc)	Membrane microfiltration (Mbr)
Filtration (Ftt)	Adsorption (Ads)	Ionic exchange (Inx)
	Disinfection (Dis)	Ultrasonic treatment (Uls)
	Membrane bioreactor (Mbrt)	Advanced oxidation process (Aop)
	Microbial fuel cell (Mfc)	
	Activated Sludge (Asl)	

3. Results: economic evaluation

The economic evaluation of the treatment process comprises capital investment and operating costs per annum. The Accelerated Branch-and-Bound (ABB) algorithm was used to generate the feasible pathways, with treatment cost ranked from least to highest. We generated 100 best solutions ranked based on costs, however, due to space limitations we have presented the detailed analysis for the first three best structures. The total annual cost of the best structure is 1,232,970 USD/y, while the cost of the third structure is just 0.03 % higher (1,233,365 USD/y). It is interesting to note that the cost of the 100th best structure is 1,341,814 USD/y, which is just 8.83 % higher than the optimal. This further demonstrates the utility of the P-graph framework, as being able to generate all feasible ranked structures with such small cost gaps which enables the designer with multiple options to account for any additional constraints.

3.1 Optimal structures

The first three feasible structures are shown in Figure 1. The optimal structure includes sedimentation (Sdm), rotating biological contactor (Rbc), microbial fuel cells (Mfc), ion exchange (Inx), and advanced oxidation processes (Aop) technologies. Stage#1, #2, and #3 are the primary, secondary, and tertiary treatment stages, respectively. The main difference between the three structures is the splitting of flows for the process. For structure#1, there is a split of 22,308 kg/h of wastewater, representing 24.77 % of the total outlet liquid stream from the ion exchange technology. From Figure 1, it can be observed that the amount of wastewater that bypasses the first stage in feasible structures #2 and #3 is minimal (0.08 % and 0.076 %). This observation can be attributed to the fact that at the primary treatment stage, the contaminant concentration within the waste stream is still high. However, the outlet stream concentrations from the secondary and tertiary stages have an appreciable amount of contaminants removed; therefore, a higher fraction of flow splitting is possible. A stagewise breakdown of the cost indicates that the tertiary stage contributes the highest with a percentage range of 65.72 – 65.73 %. The secondary stage has the least contribution with a value of 3.93 % for all the feasible structures shown in Figure 1, while the primary stage is within the range of 30.34 – 30.35 %. The further breakdown of the tertiary stage shows that the cost associated with the Aop unit is the main driving force as it contributes 93.47 % to the total tertiary treatment stage. In all cases, the chromium outlet specification was achieved. The assessment of the technologies indicates that the ion exchange unit removed over 90 % of the inlet chromium concentration.

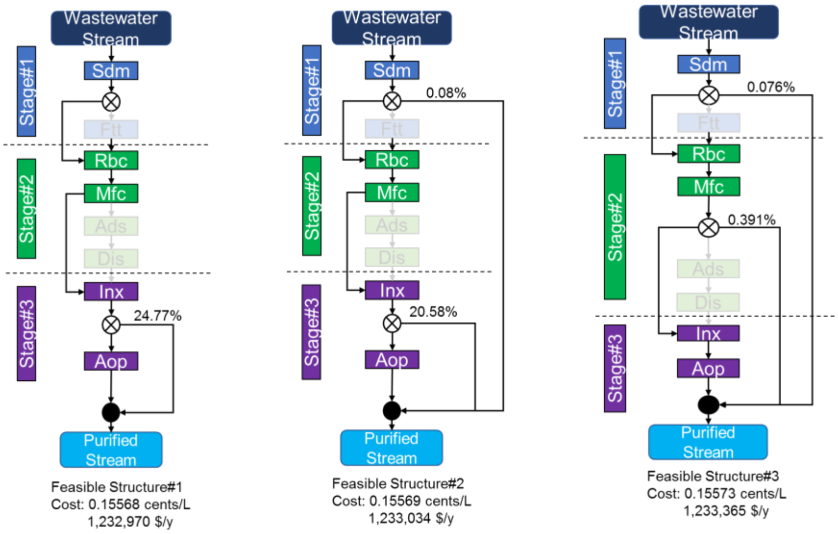

Figure 1: First three feasible structures showing the selected technologies, the cost of treatment for one liter of wastewater, and the annual cost.

3.2 Sensitivity analysis

A sensitivity analysis of the chemical contaminant flow rate for the optimal network indicates that at flows below 346 kg/h (base case), the selected structure comprises Sdm-Rbc-Inx-Aop, as shown in Figure 2. Increasing the flow rate above the base case changes the optimal network structure to Sdm-Rbc-Mfc-Inx-Aop, as shown in Figure 2.

4. Results: sustainability evaluation using the Sustainable Process Index (SPI)

The sustainable process index (SPI), developed by Narodoslawsky and Krotscheck (1995), is an ecological footprint that quantifies the environmental pressure of processes. In the context of SPI, the natural income in a sustainable economy is solar radiation. Converting solar radiation to goods and services requires area. Therefore, considering the area as a solar energy recipient and a production factor leads to SPI as a measure of the ecological sustainability of processes. The overall SPI comprises input and output areas. The input areas include raw material consumption, energy usage, area needed to accommodate stuff, and installations and infrastructure. The output areas consist of the areas required to embed air, water, and soil emissions sustainably into the ecosystem. Thus, the health impacts associated with the process are inherent within SPI analysis. In estimating the SPI for the treatment process, the amount of contaminant removed is assumed to be disposed of via land, hence considered soil emission. In addition, the purified wastewater stream is assumed to be discharged into water bodies and thus regarded as water emission. The values estimated by Aboagye et al. (2021) for the rate of renewability of the soil and water compartments of the ecosphere were used to estimate the area needed to dissipate the water and soil emissions.

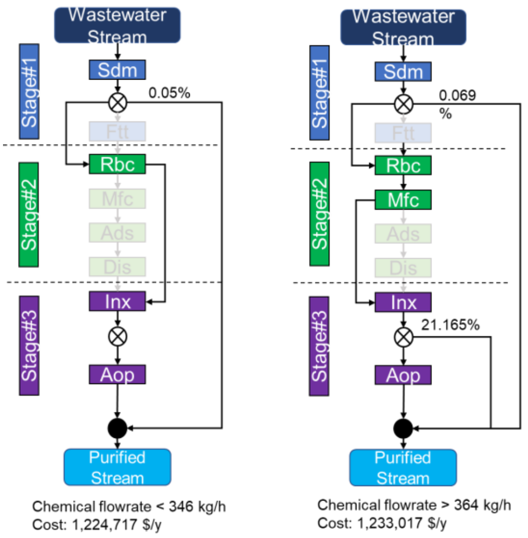

Figure 2: Effect of chemical contaminant flow variation on the optimal network.

4.1 SPI of the optimal structure & tradeoffs

Table 3 gives the SPI values per cubic meter of wastewater treated for the feasible structures shown in Figure 1. Feasible structure#1 has the least cost; however, it has the highest SPI value from the other three structures. Thus, in terms of cost, structure #1 is preferred; however, for the ecological burden, structure #2 is desired. The differences in the SPI values result from the inequality constraint applied for the outlet stream. Even though the purity requirements were achieved for all the presented structures, some achieved higher removal efficiencies.

Table 3: SPI for the feasible structures

Rank	Feasible Structure	SPI (km^2/y)	Cost ($/y)
#1	Sdm-Rbc-Mfc-Inx(24%Byp)-Aop	20.395	1,232,970
#2	Sdm(0.08%Byp)-Rbc-Mfc-Inx(20.58%Byp)-Aop	20.375	1,233,034
#3	Sdm(0.076%Byp)-Rbc-Mfc(0.391%Byp)-Inx-Aop	20.382	1,233,365
#4	Sdm-Rbc-Mfc-Inx-Aop	20.382	1,233,366

5. Conclusions

The tannery industry is one of the major polluters of the environment in terms of WW generation. To help mitigate these waste issues, efficient WW systems that consider both cost and ecological impacts must be implemented. Presented here is an integrated approach to WWTN synthesis that quantifies the cost and the environmental burden of the treatment process using the P-graph methodology. A superstructure-based optimization approach was used to consider all process flows, technologies, and mixers, thereby providing a comprehensive view of the problem. The treatment process was modeled as a mixed-integer linear programming problem, and the ABB algorithm was used in the evaluation process. The P-graph methodology provides a ranked list of feasible networks based on the cost, which is advantageous over the conventional side-by-side comparison. Based on this work it can be observed that the inclusion of SPI presents another dimension to policy-makers as feasible structures that are favorable in terms of the cost may not be beneficial with regards to their ecological pressure.

Online Resources

More resources and details regarding the structural complexity in WWTN design and the Excel-based tool for the P-graph framework proposed in this paper can be found at the P-graph community “Wastewater Treatment| P-Graph” webpage: http://p-graph.org/wastewater-treatment/

Acknowledgments

The authors would like to thank the Department of Chemical Engineering at Rowan University and the Department of Chemical and Environmental Process Engineering at Budapest University of Technology and Economics for their resources and support that assisted in the completion of this work. The research presented in this paper was funded by the “National Laboratories 2020 Program – Artificial Intelligence Subprogram – Establishment of the National Artificial Intelligence Laboratory (MILAB) at Széchenyi István University (NKFIH-870-21/2020)” project. The research contribution by H. Cabezas was carried out in the framework of the GINOP-2.3.2-15-2016-00010 “Development of enhanced engineering methods with the aim at utilization of subterranean energy resources” project of the Research Institute of Applied Earth Sciences of the University of Miskolc in the Széchenyi 2020 Plan, funded by the European Union, co-financed by the European Structural and Investment Funds. Project TKP2020-NKA-10 has been implemented with the support from the National Research, Development and Innovation Fund of Hungary, financed under the 2020-4.1.1-TKP2020 Thematic Excellence Programme 2020 - National Challenges sub-program funding scheme.

References

Aboagye E.A., Burnham S.M., Dailey J., Zia R., Tran C., Desai M., Yenkie K.M., 2021. Systematic design, optimization, and sustainability assessment for generation of efficient wastewater treatment networks. Water, 13, 1326.

Chowdhury M., Mostafa M.G., Biswas T.K., Mandal A., Saha A.K., 2015. Characterization of the effluents from leather processing industries. Environmental Processes. 2, 173–187.

Crini G., Lichtfouse E., 2018. Wastewater treatment: an overview, Green adsorbents for pollutant removal, Environmental Chemistry for a Sustainable World. Springer International Publishing, pp. 1–21, Cham, Switzerland.

Elsheikh M.A.-S., 2009. Tannery wastewater pre-treatment. Water Science and Technology 60, 433–440.

Friedler F., Tarján K., Huang Y.W., Fan L.T., 1993. Graph-theoretic approach to process synthesis: polynomial algorithm for maximal structure generation. Computers and Chemical Engineering 17, 929–942.

Friedler F., Tarján K., Huang Y.W., Fan L.T., 1992. Combinatorial algorithms for process synthesis. Chemical Engineering Science 16, Suppl. S313-S320.

Gadipelly C., Pérez-González A., Yadav G.D., Ortiz I., Ibáñez R., Rathod V.K., Marathe K.V., 2014. Pharmaceutical industry wastewater: review of the technologies for water treatment and reuse. Industrial & Engineering Chemistry Research. 53, 11571–11592.

Kundzewicz Z.W., 2007. Global freshwater resources for sustainable development. Ecohydrology & Hydrobiology 7, 125–134.

McDonald R.I., Green P., Balk D., Fekete B.M., Revenga C., Todd M., Montgomery M., 2011. Urban growth, climate change, and freshwater availability. Proceedings of the National Academy of Sciences 108, 6312–6317.

Metcalf & Eddy, Inc. revised by Tchobanoglous, G., Burton, F.L., Stensel, H.D., 2002. Wastewater engineering: treatment and reuse, 4th edition, McGraw Hill Higher Education, Boston, USA.

Narodoslawsky M., Krotscheck C., 1995. The sustainable process index (SPI): evaluating processes according to environmental compatibility. Journal of Hazardous Materials, 41, 383–397.

Saxena G., Bharagava R.N., 2016. Organic pollutants in tannery wastewater and bioremediation approaches for environmental safety. Chapter In: Saxena, G., Bharagava, R.N. (Eds.), Bioremediation of Industrial Pollutants, Educationist Press, Write & Print Publications, New Delhi, India.

Shrivastava R., Upreti R.K., Seth P.K., Chaturvedi U.C., 2002. Effects of chromium on the immune system. FEMS Immunology & Medical Microbiology 34, 1–7.

Tribe B., 2016. The U.S. hide, skin & leather fact sheet. The U.S. Sustainability Alliance. <thesustainabilityalliance.us/u-s-hide-skin-leather-fact-sheet/> accessed 6.9.21.

UNESCO, 2017. Wastewater: the untapped resource, The United Nations world water development report. UNESCO, Paris, France.

Yenkie K.M., 2019. Integrating the three E’s in wastewater treatment: efficient design, economic viability, and environmental sustainability. Current Opinion in Chemical Engineering 26, 131–138.

Yenkie K.M., Pimentel J., Orosz Á., Cabezas H., Friedler F., 2021. The P-graph approach for systematic synthesis of wastewater treatment networks. AIChE Journal 67:e17253, 1–10.