Wastewater Minimization With Differentiated Regeneration of Contaminants using Water Source Diagrams (WSD)

B.E.P.C.Delgado¹, E.M.Queiroz¹, F. L. P. Pessoa¹ *Chemical Engineering Department,* Universidade Federal do Rio de Janeiro

Av. Athos da Silveira Ramos, 149, Ed. do Centro de Tecnologia, Bloco E - Sala 201,

Cidade Universitária, CEP: 21941-909, Rio de Janeiro, RJ, Brasil, Cx Postal: 68542

tel:+552125627603, email: pessoa@eq.ufrj.br

Wastewater regeneration containing multiple contaminants involves challenges as considering the simultaneous transference of contaminants and the differentiated regeneration of these contaminants. In this work the Water Source Diagram (WSD) procedure was applied to perform the mass exchange network synthesis with differentiated regeneration of contaminants and the effluent recycle. A procedure for choosing the reference contaminant in WSD calculations was proposed. The procedure is applied in one example from literature and the results indicate a reduction of 66% in freshwater consumption.

Keywords: mass exchange network synthesis, multiple contaminants, regeneration and recycle, differentiated regeneration.

1. Introduction

Nowadays environmental law is becoming more stringent towards industrial wastewater quality discharge because of a possible water scarcity caused by pollution. Since industrial facilities require large quantities of freshwater and produce plenty of wastewater, it is important to reduce its freshwater consumption and wastewater generation which can be achieved by means of water reuse and wastewater regeneration for reuse or recycle. Regeneration and reuse or recycle allow attaining a lower freshwater consumption and wastewater production than the single water reuse. In this work the algorithmic heuristic Water Source Diagram (WSD) procedure (Gomes et al., 2007) is extended to consider the differentiated regeneration of multiple contaminants and the effluent recycle inside the plant.

2. Previous work

Takama et al. (1980) introduced the water allocation problem (WAP) in a refinery using non linear programming and considering fixed removal rates specified for each contaminant. El-Halwagi and Manousiouthakis (1989, 1990a) introduced the concept of mass exchange networks synthesis through composite curve of operations to target water flowrates based on

a graphical procedure similar to pinch technology. The problem of regeneration was solved by mathematical programming. Following pinch technology, Wang and Smith (1994) defined the water pinch concentration and targeted the minimum freshwater consumption. Wang and Smith (1994) proposed that the regeneration concentration was equal to the freshwater pinch concentration. The regeneration concentration was not identified, only the regenerated flowrate was calculated. In order to understand the changes caused by introducing regeneration, Kuo and Smith (1998) developed a new method which avoided dividing operations and allowed to take into account the regeneration equipment. Mann and Liu (1999) demonstrated by graphical method that when regeneration was applied, the system presented a regenerated water pinch concentration which can be different from freshwater pinch concentration. Mann and Liu (1999) and Hallale (2002) demonstrated that the regeneration water pinch concentration can be equal to or greater than the freshwater pinch concentration and, the post regeneration concentration should be lower than freshwater pinch concentration in order to reduce the freshwater consumption. In these works the regeneration equipment was not identified.

These methods employed a graphical approach that causes limitations for solving systems with multiple contaminants. In order to overcome these problems, Castro *et al.* (1999) proposed a procedure based on interval concentrations in which the minimum freshwater consumption and the mass exchange network synthesis were attained simultaneously. This procedure was applied in systems with single contaminant and considered only maximum reuse. An algorithm for targeting minimum freshwater consumption considering regeneration and reuse was also proposed but it resulted in dividing operations in the flowsheet. The algorithm Water Source Diagram (WSD) proposed in Gomes et al. (2007) was an extension of the procedure of Castro *et al.* (1999) and Gómez *et al.* (2000) and consisted in representing the inlet and outlet mass transfer operations in each interval.

Feng et al (2007) used the graphical method and considered a fixed post regeneration concentration. The freshwater concentration was not taken as the regeneration concentration.

None of the works in the literature has evaluated the differentiated regeneration of contaminants.

3. Problem statement: Water Source Diagrams (WSD) in problems with differentiated regeneration

Differentiated regeneration involves systems with multiple contaminants. Regeneration is applied to remove contaminants and allows the wastewater to be reused or recycled. Two approaches can be considered: fixed removal rate for the contaminant or fixed post regeneration concentration (outlet regeneration concentration) for each contaminant. As removal rates depend on regeneration and post regeneration concentrations, these concentrations can be targeted for each contaminant in order to synthesize the regeneration system for wastewater recycling and to select the equipment for treatment of each contaminant. Regeneration system synthesis or selection of regeneration equipment depends

on two initial issues: i) the choice of effluents concentration to be regenerated (regeneration concentration) and ii) the target effluent concentration after regeneration (post regeneration concentration) which makes feasible its reuse in other operations or to be recycled to the same operation, so that the freshwater consumption and wastewater generation are decreased. Regeneration cost depends mainly on regenerated water flowrate, but the regeneration water flowrate depends on the regeneration and post-regeneration concentrations (Feng et al., 2007), although these variables also influence the selection of the regeneration equipment which is represented by its removal rate. Water regeneration reduces fresh water consumption (operational cost) and increases the investment cost with equipment. The WSD synthesis with wastewater regeneration depends on the regeneration concentration or the post regeneration concentration. The proposed procedure in this work evaluates the correlation between regeneration and post regeneration concentration, targets the regeneration system removal rates, and wastewater regeneration flowrates. A specific objective in the present work is to minimize the freshwater and wastewater regeneration flowrates using the WSD diagram procedure.

4. Water Source Diagrams (WSD) in problems with differentiated regeneration

4.1Water Source Diagram (WSD) procedure

In order to solve the problem using WSD the following process data are required: i) identification of operations, ii) limit water flowrate in operations, iii) identification of contaminants, iv) maximum inlet and outlet contaminants concentrations in operations and v) contaminant concentrations in external water sources available. The WSD algorithm with maximum reuse and single contaminant follows the procedure described in Gomes et al. (2007).

4.2 Water Source Diagram (WSD) procedure with Multiple Contaminants

When multiple contaminants are present, the WSD recommends the choice of a reference contaminant for which the WSD is constructed. Then the result is extended directly proportional the concentration of contaminants in each operation. The contaminant of reference is chosen before beginning the WSD algorithm. In this work the reference contaminant is the one with the lowest inlet concentration in operations where wastewater is allowed to be used. When more than one contaminant satisfies this criterion, the final decision is made based on the difference, in each operation, for each possible contaminant of reference, according to Equation (1).

$$\Delta CR_j = C_{ff} - C_{i,m\acute{\alpha}x,j} \tag{1}$$

where C_{ff} is the outlet concentration of contaminant j originating in operation that uses freshwater and $C_{imax, j}$ is the maximum inlet concentration of contaminant j at the operation where it will be reused, and ΔCR_j is the difference in concentration of each contaminant j.

The reference contaminant is the one with lowest value of ΔCR_j in order to priority water reuse with higher contaminant concentration.

Once the reference contaminant is chosen, the inlet and outlet concentrations are recalculated in order to consider the simultaneous transference of contaminants when water is reused. In this procedure a rate of mass transfer is maintained between the contaminants in each operation, as well as the mass transferred of each contaminant in the operation. This concentration displacement follows the same heuristic rules as proposed by Wang and Smith (1994).

4.3 WSD algorithm with differentiated regeneration – Multiple Contaminants and Minimum Inlet Concentration (MIC)

The proposed procedure is based on a fixed post regeneration concentration In WSD synthesis the regeneration process can be considered as a search for the minimum freshwater consumption and minimum regenerated water flowrate. Regeneration is applied to remove contaminants in an intermediary process, generating a treated wastewater with concentration equal to C_o . A single or combined treatment processes can be used to generate treated wastewater. The treated wastewater represents a new water source available to be reused or recycled in the WSD synthesis. In the present work, the post regeneration concentration (C_o) for the reference contaminant is fixed and equal to the minimum non zero inlet concentration. The differentiated regeneration of an effluent stream containing multiple contaminants generates a source of regenerated water with different outlet concentration for each contaminant.

Regeneration can be centralized or distributed according to the mixture or not of effluents. In the case of centralized regeneration the effluent are mixed. On the other hand, they are mixed or not. In this work the WSD synthesis considered only the distributed regeneration of effluents. Some effluents are mixed upstream regeneration when indicated in WSD, but it does not include all effluents streams as used in the centralized end of pipe treatment.

The WSD with differentiated regeneration procedure is described in 8 steps.

Step1: Chose the reference contaminant following Equation (1), and, if necessary, adjust the maximum inlet and outlet concentrations.

Step2: Construct WSD for maximum reuse (Gomes et al., 2007) and determine the *pinch* concentration. In the WSD for maximum reuse, select the effluents, whose concentration is higher than pinch concentration, to be regenerated.

Step3: Construct the WSD for regeneration and recycle after setting up the post regeneration concentration (C_o) as the lowest non zero inlet concentration (C_o) represented in the WSD, in order to keep the inlet concentration in each operation below the maximum limited and guarantee the minimum freshwater consumption. Notice that the lower the effluent is compared to the minimum inlet concentration (C_o) , the lower is the regenerated flowrate and the higher is the removal. However, to allow wastewater to be recycled it just need to have a concentration equal to the minimum inlet concentration (C_o) . On the contrary, if the effluent is regenerated to a higher concentration than (C_o) , the regenerated water flowrate increases in order to comply with the recycling and the removal rate is reduced. As a result, the total

flowrate in an operation could increase and the mass exchange network would be infeasible (Gómez et al., 2001). The regenerator removal rate is specified using C_o and the contaminant concentration in the effluent that will be reused or recycled. The WSD with regeneration synthesis for a single contaminant follows as described in Gomes et al. (2007). **Step 4:** Perform the mass exchange network (MEN) synthesis with data relative to reference contaminant and the respective WSD for regeneration and recycle from Step 3. Calculate the contaminants concentrations in all operations of the mass exchange network based on WSD flowrates for the reference contaminant and maintaining the quantity of mass changed in

Step5: In case of violation of the maximum inlet or outlet concentrations in the mass exchange network, adjust the freshwater flowrate to satisfy the criterion of maximum inlet and outlet concentrations or include a regenerator to these contaminants with concentrations out of specifications. Although a new regenerator increases the investment cost, the operational cost with end of pipe treatment is reduced because the recycled wastewater decreases the final effluent flowrate.

Step6: Construct the final MEN using information about contaminants concentrations in Step 5, including new regenerators, if necessary, or adjusting the freshwater and regenerated water flowrates in operations. The new regenerators removal rate (*RR*) are calculated to allow the mass transference of contaminants in operations according to the contaminant concentrations calculated in each operation. Once with all contaminant concentrations, calculate each contaminant removal rate, using Equation (2):

$$\%RR = \frac{C_{ER} - C_{ENTJ}}{C_{ER}} x100 \tag{2}$$

where C_{ER} is the effluent concentration that will be treated, C_{ENTj} is the maximum contaminant j inlet concentration in the operation where the effluent will be reused and RR is the target regenerator removal rate.

Step7: Verify among the regenerators available for each contaminant, the treatments that satisfies the contaminants removal rates established in Step 6. Create a list of regenerators available for each contaminant. The selection of a regeneration processes can be based on the desired removal rate and the contaminants identification in the effluent. The synthesis of the regeneration system consists in selecting the treatments which have a removal rate greater than or equal to the specified contaminant removal rate in the MEN and/or the treatment with the lowest cost. In this work the treatment costs are based on the wastewater treated flowrates.

Step8: Perform the synthesis of the MEN with the regeneration system using the regenerators according to the desired removal rate for each contaminant. In case of the treatment removal rate being greater than the desired value, the regenerator outlet concentration will be lower than C_o, and the regenerated water flowrate in an operation will be reduced in the final mass exchange network. It is recommended that the treatment with

the highest removal rate is selected in order to treat the lowest regenerated water flowrate and to reduce operational costs with regeneration. More than one regenerator can be used to perform the regeneration system synthesis in order to satisfy the targeted removal rates. The final regeneration concentration and removal rates are the main outputs in the final mass exchanged network synthesis. The regeneration concentration is different from the freshwater *pinch* concentration because some effluents can be mixed before entering the regeneration process and the presence of more than one contaminant leads the flowrates to be adjusted so that the maximum contaminants concentrations in operations are obtained.

5. Results and Discussion

The proposed procedure was applied to several examples, but only one will be present. The example was taken from Takama et al (1980). Oil was the reference contaminant following Equation (1). Table 1 are shown the data with the maximum inlet and outlet contaminant oil concentration accordingly adjusted (following Eq(2)) in operation 3 (desalter).

Table 1 – Problem data with contaminant oil concentration adjusted

Operation	f _k (t/h)	Contaminant	C _{ik,max} (ppm)	C _{fk,max} (ppm)	$\Delta m_k (kg/h)$
1 Steam strippers	45.8	H ₂ S	0	390.8	17.9
		Oil	0	10.9	0.5
		SS	0	26.2	1.2
2 HDS	32.7	H_2S	500	16891.4	536
		Oil	20	120.9	3.3
		SS	50	65.3	0.5
3 Desalter	56.5	H_2S	20	43	1.3
		Oil	0.5587	101.5	5.7
		SS	50	85.4	2.0

Figure 2 shows the WSD for regeneration and recycle. The freshwater pinch concentration was 101.5 ppm oil. The post regeneration concentration (the lowest maximum inlet concentration operation (C_0)) is 0.5587 ppm oil. The freshwater consumption is 45.8t/h as shown in the first interval concentration. Effluents from operations 2 and 3 present a higher concentration than the freshwater pinch concentration (101.5 ppm) and can be sent for regeneration. Figure 3 shows the final mass exchange network for regeneration and recycle. The maximum inlet and outlet concentrations of H_2S and SS were exceeded in operation 3 (Step 5). Then a regenerator for contaminants oil, H_2S and SS was included before entering operation 3. The minimum percent removal rates for regeneration of these contaminants are 99.2% for oil, 85.7% for H_2S and 27% for SS (Step 6).

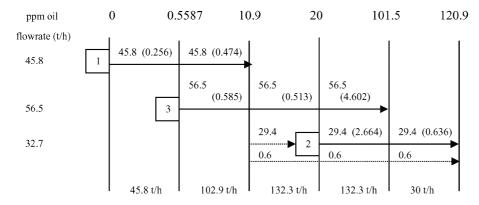


Figure 2 – WSD for regeneration and recycle

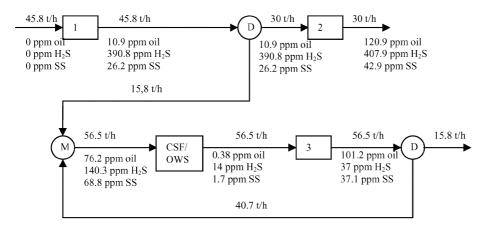


Figure 3 – Mass exchange network for regeneration and recycle with regeneration system.

The available treatments for contaminants oil, H₂S and suspended solids (SS) with respective removal rates were taken from Takama et al. (1980). Oil-water separator (OWS) and coagulation, sedimentation and filtration (CSF) are selected to construct the system of regeneration as shown in Figure 3 (Steps 7 and 8). The maximum inlet and outlet contaminants concentrations were not violated. The freshwater flowrate was reduced with regeneration and recycle from 135t/h to 45.8t/h (66%) and the regenerated water flowrate (113t/h) was minimized with the proposed procedure. Economic evaluation showed a total annual cost reduction from 324,000 \$/year to 151,489 \$/year (53%) in relation to the initial problem and 19.4% in relation to maximum reuse. Treatments were selected according to

the contaminant and the specified removal rate to allow the effluent to be recycled. Note that the regeneration concentration is 76.2 ppm oil as shown in Figure 3.

6. Conclusions

The proposed procedure do not considered the same fixed post regeneration concentration for all contaminants as in Gomes et al (2007). Regeneration pinch concentration is different from freshwater pinch concentration when the mass exchange network synthesis is carried out considering a certain post regeneration concentration for the reference contaminant. The regeneration pinch concentration (76.2 ppm oil) is calculated in the final mass exchange network and, in this example, it is lower than the freshwater pinch concentration (101.5 ppm oil). The proposed procedure yielded a freshwater water reduction (66%) greater than the one from literature (24%) both with rather similar values for the total annual cost reduction, 53% and 55%, respectively. Note that each contaminant in the effluent stream has a different removal rate in the regeneration system of the mass exchange network. If more than one treatment is applied to the same stream, the procedure does not establish the sequence of treatments, and it is suggested as a future work.

7. References

- Castro, P., H. Matos, M.C. Fernandes and C.D. Nunes, 1999, Improvements for mass-exchange networks design. Chemical Engineering Science, 54, 1649.
- El-Halwagi, M.M. and V. Manousiouthakis, 1989, Mass exchanger networks. AIChE Journal, 35 (8), 1233.
- El-Halwagi, M.M. and V. Manousiouthakis, 1990, Automatic synthesis of mass exchanger networks with single component targets, Chemical Engineering Science, 45 (9), 2813.
- Feng, X., J. Bai and X. Zheng, 2007, On the use of graphical method to determine the targets of single-contaminant regeneration recycling water systems, Chemical Engineering Science, 62, 2127.
- Hallale, N., 2002, A new graphical targeting method for water minimization, Advances in Environmental Research, 6, 377.
- Gomes, J.F.S., E.M. Queiroz and F.L.P. Pessoa, 2007, Design procedure for water/wastewater minimization: single contaminant, Journal of Cleaner Production, 15, 474.
- Gómez, J., M. Savelski and M. Bagajewicz, 2001, On a systematic design procedure for single component water utilization systems in process plants, Chemical Engineering Communications, 186, 183.
- Kuo, W.C.J. and R. Smith, 1998, Designing for the interactions between water-use and effluent treatment, Transactions of International Chemical Engineering, 76 Part A, 287.
- Mann, J.G. and Y.A. Liu, 1999, Industrial Water Reuse and Wastewater Minimization, McGraw Hill, New York.
- Takama, N., T. Kuriyama, K. Shiroko and T. Umeda, 1980, Optimal water allocation in a petroleum refinery, Computers and Chemical Engineering, 4, 251.
- Wang, Y. and R. Smith, 1994, Wastewater Minimization, Chemical Eng Science, 49, 981.