

Abstract

The protection of continuous drinking water supply is really important all over the world, also in Hungary. Many kinds of hazardous chemicals could pollute the natural water resources, arsenic is one of the most occurring pollutant in Hungary. Recently, an ethylene-vinyl alcohol copolymer based arsenic removal adsorbent has been developed. During the manufacturing process hazardous waste water is produced, which is burned in the incineration plant, so this open production process needs fresh solvent every time. However, if the different fraction of the waste water is separated by distillation both the volume of the hazardous waste water can be reduced extremely and the recovered solvent and water can be reused in the manufacturing process. Beside analytical measurements Life Cycle Sustainability Assessment (LCSA) was prepared to identify and compare the environmental, economic and social effects of the current technology and the new one. The results proved that the technology closed by distillation is better than the current open one in each aspect of LCSA.

Keywords

DMSO, solvent recovery, sustainability analysis, life-cycle assessment

1 Introduction

The protection of clean water is one of the major challenges of environmental actions all over the world. The reservation of potable, unpolluted water base is fundamentally important for continuous production of drinking water as well as for agriculture utilization. Although Hungary has a large amount of good quality natural water resources, in some area of the country (Fig. 1), several hazardous or even toxic chemicals *i.e.* arsenic, ammonia, boron, manganese could be found in the water reserves, which have to be removed to produce drinking water. [1] In order to remove these pollutant species from raw water, several robust technologies such as chemical precipitation, flotation, adsorption, ion exchange, membrane filtration and electrochemical deposition have been developed [2].

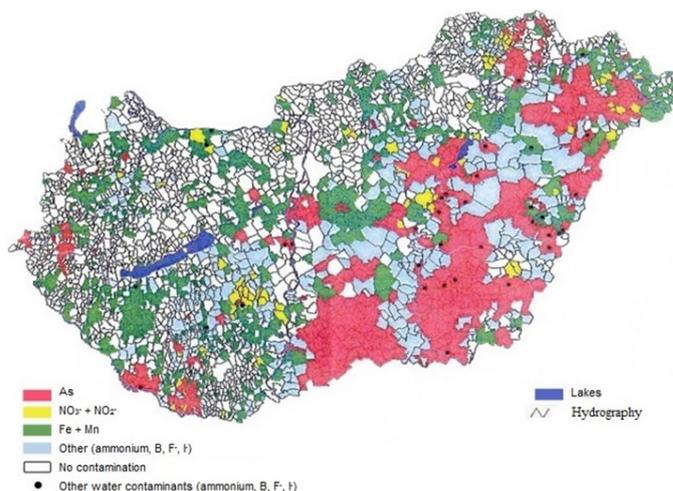


Fig. 1 The most hazardous contaminants in drinking water in Hungary [1]

Arsenic is a naturally occurring metalloid having very high mobile in the environment. It is known to be highly toxic to all life forms [3] and has been classified by the World Health Organization (WHO) as a group 1 human carcinogenic substance [4]. Consequently, its removal from water is a widely studied important issue for producing drinking water [5]. Among these removal processes adsorption techniques are generally preferred due to the possible regeneration and therefore the reuse of the solid phase. Recently, an ethylene-vinyl

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alcohol copolymer (EVOH) based arsenic removal adsorbent has been developed by S-Metalltech 98. Ltd, Szentendre, Hungary. It is able to remove both As(V) and As(III), furthermore on industrial scale and no any auxiliary components or considerable energy are necessary. The lifetime of this polymer is determined as seven years. The manufacturing process of polymeric adsorbent resulted waste water containing 20 wt% dimethyl sulfoxide (DMSO), from which the DMSO separation and recycling in the production of adsorbent is highly desired to reduce the environmental impact of the technology. However, lack of studies is reported on the efficient DMSO recovery from waste waters. Four potential waste water treatments were analyzed: two of them are on simulation stage [6], [7], one is in laboratory level [8], and one of these is used widely [9].

In the study of Cho and Kim [6], computer modelling and comparative study were performed resulting in pure DMSO from a mixture containing methanol, water and DMSO for two different distillation sequences. NRTL liquid activity coefficient model was used for the modeling of each binary vapor-liquid equilibrium for DMSO, methanol and water systems [6]. Anjaiah Nalaparaju and Jianwen Jiang [7] prepared molecular simulation study which is reported related to the recovery of DMSO from aqueous solutions in three hydrophobic Metal–Organic Frameworks (MOFs), namely $Zn_4O(bdc)(bpz)_2$, $Zn(bdc)(ted)_{0.5}$ and ZIF-71. According to simulations study these hydrophobic MOFs are highly selective towards DMSO adsorption from DMSO/H₂O mixtures so they are superior candidates for DMSO recovery [7].

Ravikumar and co-workers [8] evaluated the technically and economically feasible solution to recover the 15-21 wt% DMSO content from pharmaceutical waste water, which contains hazardous sodium azide too. Due to the hazardous components a hybrid methodology were applied as follows: i) inorganic salts from the pharmaceutical effluent were removed by electrodialysis; ii) the DMSO content was recovered by a two-step distillation process with desired purity and quantity. However, it should be noted that this technology has not been applied in industrial scale yet [8].

The Gaylord Chemical Company, L.L.C. developed a complex methodology to separate DMSO from aqueous solution. In this case the DMSO content of the technological waste water was 10-20 wt% and it was recovered as follows. Initially, the DMSO-water solution was concentrated up to 40-70 wt% organic content, followed by removal of all volatile compound by evaporation (p: vacuum, pH adjustment prior to evaporation) and DMSO was then separated from water by fractional distillation (p: vacuum, T_{bottoms} : 120-150 °C) [9].

Herein we report on the evaluation of concerns of each methodology and according to the SWOT analysis of the different technologies the optimal waste water treatment, which is the most adaptable for the existing manufacturing process in point of economy and efficiency, is the Gaylord-methodology.

2 Material and methods

To determine whether the new waste water treatment, namely the distillation, will reduce the environmental, economic and social impact of the technology, we applied different methods, mainly experimental, analytical and simulative ones. The applied methods are the followings:

- Analytical measurements: qualitative and quantitative analysis of waste water, and also the different separated fractions (water, solvent /DMSO/ and other components), furthermore the comparing is mostly based on descriptive statistics (for example relative standard deviation); components was determined with GC-FID (equipment: Agilent 7890 A, column type: ZB-624 (30 m, 250 μ m, 1.4 μ m), carrier gas: hydrogen, injection method: split 200:1, T_{injector} : 220 °C, v: 1.08 ml/min, detector: FID, T_{detector} : 220 °C), Karl Fischer titration (equipment: Metrohm 684 KF Coulometer, reagent: Aqualine™ Electrolyte AD-G Karl Fischer coulometric reagent) and the measurements were prepared according to the following standards: MSZ 318-3:1979, ISO 7888:1985, MSZ ISO 6060:1991, MSZ 1484-22:2009, EPA 8260 C:2006 and MSZ EN ISO 12937:2001 [10-15]. The quality of the extracted water was compared to the figures stated in Annex 4 of Hungarian regulation No. 28/2004 (XII. 25.).
- Sustainability analysis: which is mostly based on Life Cycle Sustainability Assessment (LCSA) which includes the Environmental Life Cycle Analysis (E-LCA), the Life-Cycle Cost (LCC) and the Social Life Cycle Assessment (S-LCA) and with this method it is possible to compare the environmental, economic and social impacts of the linear and new closed technology and to determine the criteria of sustainability. The solvent recycling meets with the new initiative of European Environmental Policy as „the Circular Economy” as achieve a new way towards the green and sustainable economy. According to the European Union action plan for „the Circular Economy”, the overall objective of resource efficiency can be achieved only through the implementation of circular economy, where the value of products, materials and resources is maintained in the economy for as long as possible, and the generation of waste is minimized [16]. So in this view the LCSA provides more adaptable information regarding the sustainability of a development, as with Life-Cycle Assessment (LCA) it is able to assess environmental impacts associated with all the stages of a product’s life but with LCSA it is possible to determine not only the environmental impacts but also the economic and social effects too. In this work the assessment is based on ISO 14040 standard, SimaPro 7.2 demo and GaBi 4 programs were applied, furthermore Ecoinvent database and CML 2001 method was used to evaluate the effects, the applied impact category indicators were

Abiotic Depletion Potential, Acidification Potential, Eutrophication Potential, Global Warming Potential, Human Toxicity Potential, Ozone Depletion Potential, Photochemical Ozone Creation Potential. The goal of the LCSA was to evaluate the environmental, economic and social impact of the closed technology. The functional unit was 1 m³ adsorbent. The system boundaries were determined from gate to waste treatment. First of all technological data and experimental results were used, any other additional information came from Ecoinvent database or literary sources. Two scenarios were determined: in the first one the recovery of DMSO takes 98% (DMSO_R'), in the second one beside this recovery it is used renewable resources too (DMSO_R'+PV).

With these methods the waste water itself and the separated fractions by distillation (both at laboratory level and at testing phase) were analyzed, therefore it was possible to compare the estimated, laboratory and operating results as well.

3 Results and discussion

The waste water beside 20 w/w% DMSO contains: soluble polymer – ethylene-vinyl alcohol copolymer (EVOH) and minerals such as cerium-hydroxide. In the current situation this waste water needs to be collected and transferred to the incineration plant to be burned, so the transferred DMSO needs to be replaced with fresh solvent in the production process. Fig. 2 shows the different steps of the manufacturing process with the material flows, so the conclusion can be drawn that the current process is a linear, open technology.



Fig. 2 The current manufacturing process (open technology)

If the manufacturing process is supplemented with the new waste water treatment, namely with distillation, the open technology turns into closed one (Fig. 3), and it is possible to reuse the separated water and also the solvent in certain steps of the manufacturing process, reducing the amount of the input materials, furthermore only the rest (1-2%) of the waste water needs to be transferred to the incineration plant.

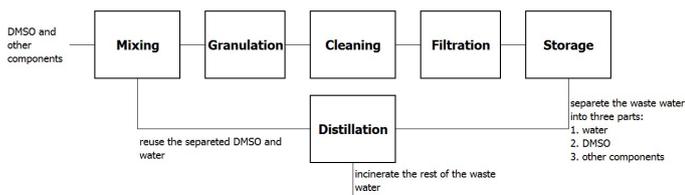


Fig. 3 The planned manufacturing process (closed technology)

The qualitative and quantitative analysis of the waste water has been prepared, Table 1 summarizes the most important

attributes of the waste water. The relative standard deviation (RSD), which is defined as the ratio of the standard deviation to the mean, describes the collection of information and it confirmed the representativeness of the sample. The qualitative and quantitative analysis of the waste water strengthened that the optimal solution for reducing the volume of the hazardous waste water and reusing the recovered solvent and water in the production process is distillation.

Table 1 Summary table about the most important attributes of the waste water

Attributes	pH	COD (mg/l)	Ce content (mg/l)	DMSO content (w/w%)	Residue on ignition (g/l)
Mean	3.53	63 000	0.25	20.9	1.39
Deviation	0.74	10 000	0.06	1.6	0.08
Minimum	2.61	49 000	0.12	17.5	1.24
Maximum	4.52	81 000	0.32	22.2	1.58
RSD	0.21	0.17	0.24	0.07	0.06

Then the waste water was separated by distillation at laboratory level (p= 5 kPa, in the first step: T_{bottom}: 102 °C, T_{top}: 89 °C, in the second step: T_{bottom}: 124 °C, T_{top}: 100 °C) and in testing phase (p= 5 kPa, in the first step: T_{bottom}: 58 °C, T_{top}: 32 °C, in the second step: T_{bottom}: 85 °C, T_{top}: 32 °C, v_{feed}: 120 l/h, v_{overhead}: 95 l/h, reflux ratio: 1.74, number of theoretical plate: 7, packing type: Sulzer Structured packing, type Mellapak Plus 452 Y) and the quantity and quality of the overhead and bottoms product was analyzed. So it was possible to draw conclusion regarding the efficiency of distillation from the qualitative composition of the different fractions (water, solvent /DMSO/ and other components).

Parallel the sustainability analysis was preparing and continuously updating with fresh results, the evaluating method was Life Cycle Sustainability Assessment (LCSA). First the environmental impact of the solvent was analyzed and the results in the two different scenarios were compared with the original data related to DMSO. Table 2 shows the values in each impact category.

Table 2 Comparing environmental impacts of the DMSO (from database) with the results in scenario 1 (DMSO_R') and in scenario 2 (DMSO_R'+PV) (characteristic factors/1kg)

	DMSO	DMSO_R' (scenario 1)	DMSO_R'+PV (scenario 2)
ADP[kg Sb eq]	0.021	0.004	0.002
GWP [kg CO ₂ eq]	1.272	0.569	0.395
ODP [kg CFC ₁₁ eq]	1.76E-07	3.48E-08	2.39E-08
AP [kg SO ₂ eq]	0.054	0.002	0.001
EP [kg PO ₄ eq]	0.002	0.001	0.001
HTP [kg 1,4-DB eq]	1.083	0.345	0.059
POCP [kg C ₂ H ₄]	1.00E-03	1.07E-04	7.18E-05

Fig. 4 shows more graphically the significant differences in each impact category, so according to the results of the life cycle assessment it is possible to draw the conclusion that the environmental effect is significantly decreased if the solvent is recovered and reused in the manufacturing process.

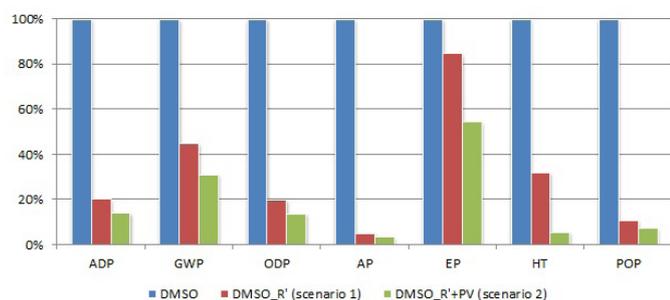


Fig. 4 Comparing environmental impacts of the DMSO (from database) with the results in scenario 1 (DMSO_R') and in scenario 2 (DMSO_R'+PV)

However with the Life Cycle Sustainability Assessment (LCSA) it is able to analyze not only the environmental impacts (Environmental Life Cycle Analysis, E-LCA), but also the economic (Life-Cycle Cost, LCC) and social (Social Life Cycle Assessment, S-LCA) effects too. According to these, the criterion of sustainability is the following:

$$\begin{aligned} LCSA_{open} & (= E - LCA + LCC + S - LCA) > \\ LCSA_{closed} & (= E - LCA + LCC + S - LCA) \end{aligned} \quad (1)$$

Therefore it is needed to take into account the inventory of the whole process in the linear open and the new closed technology to define and compare their environmental, economic and social impacts. If the values of all the three aspects in the closed technology are more favorable than in the open one, the planned development contributes the sustainability. Fig. 5 shows Life Cycle Sustainability Assessment of the technologies: open, closed and closed one with 50% renewable energy sources.

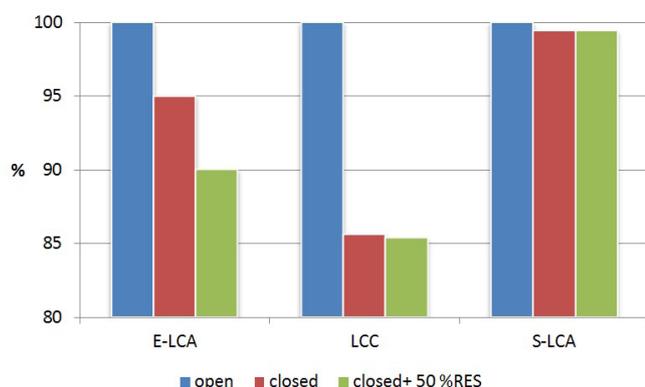


Fig. 5 Life Cycle Sustainability Assessment of the different technologies

In case of the E-LCA the other component of the waste water, for example the cerium, has higher environmental effect than the DMSO, therefore the impact of the solvent recovery

is not so significant. The most significant differences are in the Abiotic Depletion Potential (ADP), Global Warming Potential (GWP), Eco-toxicity Potential (ETP) impact categories.

In case of the LCC the nearly 15% decreasing, namely cost reduction, is caused mostly by the high price of the solvent, because if it is possible to reuse as much solvent as we can by distillation it is needed to buy little amount of fresh solvent. The ratio of the cost reduction from the technology development (reusing the recovered water and solvent, less amount of hazardous waste) and the increased expenses (arisen energy and water demand) was analyzed and the financial saving of the development is 17% of the total costs.

In case of the S-LCA it is possible barely to observe the effect of the new, closed technology in both of the two scenarios. In this view of the LCSA it was taking into account that the number of employees is not changed and the comparing is based only on the rate of the salaries and total production costs. As the amount of the salaries is much smaller than the total production costs, the effect of the open and closed technologies is almost the same. However it is important to monetize the other impacts of the closed technologies, such as increased value added, increased professional knowledge/competence, better working circumstances, but it is a big challenge due to these are subjective elements.

4 Conclusions

In this work Life Cycle Sustainability Assessment was performed to demonstrate that the solvent recovery in manufacturing technology of EVOH-based adsorbent reduces the environmental, economic and social impact of the production. To conclude:

- the amount of hazardous waste water could be reduced from 265.2 ton/year to 5.5 ton/year, so with 98%;
- the amount of water used in the manufacturing process could be reduced approximately with 27%;
- the reused amount and the purity of the DMSO solvent depends on the efficiency of the distillation process, the objective is approximately 98% purity. The results of measurements in laboratory scale confirmed our preliminary estimates, for example the purity of the recovered DMSO by distillation is at least 95%, and minimum 78% of the input solvent can be reused in the manufacturing process again, moreover on the basis of the results in the testing phase it is possible to reuse more than 85 % of the input solvent in a really high purity.

According to these results it is able to set out that the LCSA can be a possible solution to identify the sustainability of the future developments. Moreover the LCSA of this study proved that there is reason for existence of such circular technology as industrial ecological model in national practice.

Abbreviations

ADP	Abiotic Depletion Potential
AP	Acidification Potential
DMSO	dimethyl sulfoxide
E-LCA	Environmental Life Cycle Analysis
EP	Eutrophication Potential
ETP	Eco-toxicity Potential
EVOH	ethylene-vinyl alcohol copolymer
GWP	Global Warming Potential
HTP	Human Toxicity Potential
LCA	Life-Cycle Assessment
LCC	Life-Cycle Cost
LCSA	Life Cycle Sustainability Assessment
ODP	Ozone Depletion Potential
POCP	Photochemical Ozone Creation Potential
RSD	relative standard deviation
S-LCA	Social Life Cycle Assessment

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