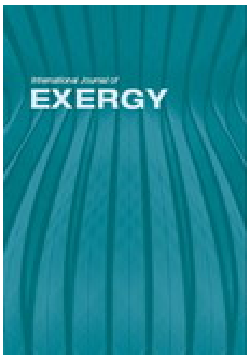

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Exergy analysis of purified water plant in a pharmaceutical industry

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Abstract: Thermodynamic optimisation of manufacturing plants at design or operation stages is known to be a complex process, resulting from the consideration of various design and operation parameters. Exergy analysis is an appropriate tool to implement the thermo-economical optimisation of processes in a convenient way. In this study, exergy analysis was applied to a purified water (PW) plant in the pharmaceutical industry composed of various units such as ultrafiltration (UF), activated carbon columns, softener columns, reverse osmosis (RO), degasser, and continuous electro deionisation unit (CEDI) process, and the exergetic efficiencies were found to be 75.47%, 84.70%, 64.78%, 37.67%, 96.88% and 85.50%, respectively. Considering the exergetic efficiency of the entire plant of 4.35%, significant opportunities are available to increase the energy and exergy efficiencies of this PW plant by means of structural as well as parametric optimisation tasks. By considering that most of the energy destruction in this plant stems from pump motors, especially in the RO unit, energy recovery devices such as pressure ex-changers and Pelton wheels may be used to increase the energy efficiency of the plant.

Keywords: desalination; exergy; pharmaceutical industry; plant performance.

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1 Introduction

Conventional thermodynamic analysis of material processing or transfer of energy is based on the first law of thermodynamics, which is the conservation of energy. The first law is used to reduce heat loss or to increase the recovery of heat waste, but it cannot tell you how much energy was used during the process.

The most effective way to increase the energy economy in a manufacturing plant is to use the energy in an efficient way. In this context, energy analysis, based on the second law of thermodynamics, defines points and magnitudes of energy degradation and inefficient natural resource utilisation (Kotas, 1986, 2013; Dincer and Cengel, 2001), and is thus successfully applied in a variety of engineering fields (Kotas, 1985, 2013; Sahin et al., 2015; Szargut et al., 1988; Tekin and Bayramoglu, 1998).

In the literature, there are various exergy definitions (Kotas, 1985, 2013; Szargut et al., 1988; Tekin and Bayramoglu, 1998). Among these definitions, the most general one is that the obtainable maximum quantity of work during the steady stream of matter from its initial state to the thermodynamic state of the environment is determined by the processes interacting with the environment (Szargut et al., 1988).

The main energy components are classified as physical, chemical, kinetic, and potential terms, excluding nuclear, magnetic, electric, and interfacial effects. Thus, the total specific exergy flow is written as (Szargut et al., 1988; Taufig et al., 2007; Tekin and Bayramoglu, 1998);

$$e=(h-h_0)-T_0(s-s_0)+e_{ch}+\frac{v^2}{2g}+(z-z_0)g \tag{1}$$

For exergy analysis of chemical processes, kinetic and potential components are usually left out, which is a mixture of pure solids and liquids:

$$e_{ch}=\sum\nolimits_i w_i e_{ch,i}^0 \tag{2}$$

where e_{ch}^{0} denotes the chemical exergy of a pure component at a dead state. For liquid or solid solutions:

$$e_{ch} = \left(\sum x_i e_{ch,i}^{0} + RT_0 \sum x_i \ln\left(\alpha_i\right)\right) / M \tag{3}$$

For dilute solutions, the activity a_i is equal to γ_i, x_i, x_i for solvent and equal to $\gamma_m M_i$ for solutes.

The conservation of energy is only observed for reversible processes. For real processes, a loss term, *I*, is required to account for irreversibility. For a steady-state flow system, the energy balance is written in the following form (Kotas, 1985, 1986; Szargut et al., 1988; Tekin and Bayramoglu, 1998):

$$\sum_{in} me + W + \sum_{in} E^{Q} = \sum_{out} E^{Q} + I \tag{4}$$

where E^{o} denotes the exergy of heat Q_h transferred from or to a heat source:

$$E^{Q} = Q_h \left(1 - \frac{T_0}{T_h}\right) \tag{5}$$

The exergetic performance of systems is evaluated by considering different criteria. The exergetic or rational efficiency is expressed as:

$$\begin{aligned} \varnothing &= \frac{Useful\ exergetic\ effect}{Driving\ exergy} \\ &= \frac{\sum_{out} (me)_{p-} \sum_{in} (me)_{r}}{mfef + W + \sum_{out} E^{Q}} \end{aligned} \tag{6}$$

As for the cumulative degree of performance, it is defined as the ratio of the sum of useful product exergies to total energy given to the system by means of energetic (fuel) and non-energetic raw materials (Szargut et al., 1988; Tekin and Bayramoglu, 1998):

$$\begin{aligned} \eta &= \frac{\sum (Exergies\ of\ useful\ products)}{Feeding\ exergy} \\ &= \frac{\sum_{out} (me)_p}{\sum_{in} (me)_r + mfef + W + \sum_{in} E^{Q}} \end{aligned} \tag{7}$$

η is the suggested criterium for assessing the thermodynamic efficiency for chemical processes.

However, for thermal and separation processes such as heating and cooling or distillation, is a more appropriate performance parameter because its definition eliminates the effects of chemical exergy on performance. In other respects, the chemical exergies of main and by-products can put into the state the effect of inherent irreversibility on the exergetic efficiency of the process.

It is predicted that the European pharmaceutical market will increase by 3.9% between 2019 and 2024; likewise, the global market is expected to rise by about 4.2% in the same period (Nellessen et al., 2021). Water is crucial for the production of pharmaceutical ingredients, intermediates, and final products, as well as for the purification and preparation of reagents.

However, water used for pharmaceutical applications is subject to strict regulations. Within the current pharmacopoeias, a distinction is made between PW and water for injection (WFI) (Nellessen et al., 2021). PW is used for the production of medical products that are neither pyrogen-free nor sterile. Pyrogens are substances that can cause fever in humans during parenteral intake (bypassing the intestine, e.g., intravenously). WFI is water for the production of medical products, solutions, and dilutions for parenteral use. Drinking water of sufficient quality according to the respective national regulations is the raw material for both PW and WFI production (Nellessen et al., 2021). In the European Union, the quality of water for the pharmaceutical industry, as determined by the European Pharmacopeia (Ph. Eur), can be provided using desalination processing. These processes are implemented by two major principles, which are evaporation and condensation, and filtration (Gude et al., 2010; Gude, 2015; Mistry et al., 2011; Shatat and Riffat, 2014). Any evaporation process necessitates thermal energy to obtain pure water vapour from a saline water source. This water vapour is condensed on a cooling surface to produce fresh water. A desalination process is also carried out by a membrane, which is a physical barrier to produce water molecules from saline water through permeation or diffusion. The study reported that the best desalination process given exergetic efficiency was RO, with an efficiency of 31.9%, while those of other desalination processes were much lower, typically 2.9% (multi-stage flash distillation), 5.9% (multi-effect desalination), 8.5% (mechanical vapour compression), 1% (direct contact membrane) and 2.4% (humidification-dehumidification) (Mistry et al., 2011; Sadri et al., 2016).

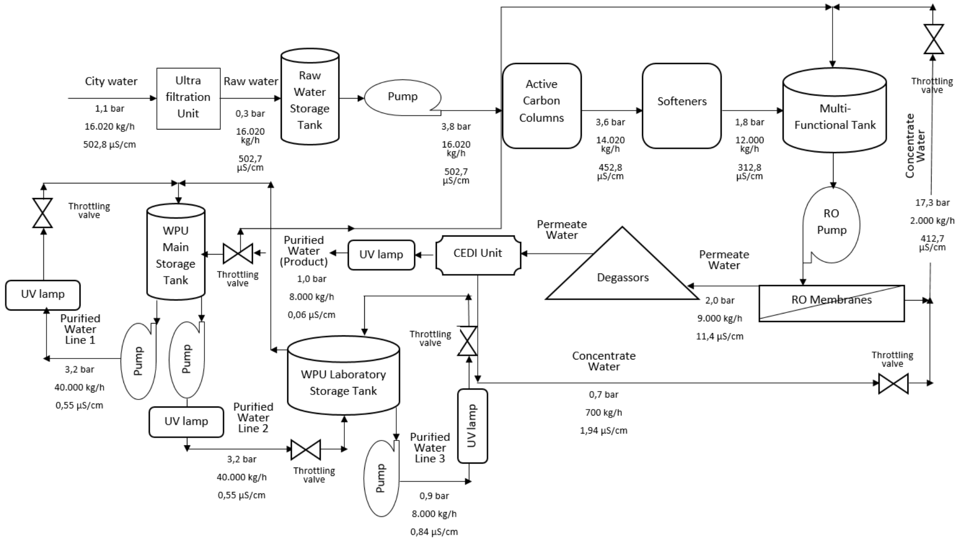
To the best of our knowledge, in the literature, there is no application of the exergy analysis to the plant producing PW for the pharmaceutical industry, which requires more desalted and sterile water, unlike other effluents of desalination plants. Therefore, the aim of this study is to apply energy analysis to a PW plant with a capacity of 192 m^3/day in the pharmaceutical industry to determine the thermodynamic efficiency of each treatment unit and the entire plant.

2 The purified water plant

Unlike water, PW does not contain any inorganic compounds. Therefore, water purification is the process that removes ions from water. The use of PW, produced by various desalination technologies, is expended in various industries such as pharmaceuticals, the health sector, cataphoresis, galling, textile and automotive. Among these sectors, in pharmaceutical factories to be operated according to current good manufacturing practice (CGMP), PW is indispensable as a primary component due to being used as the most important raw material, for cleaning of equipment/systems and also as an additive material in production. In the pharmaceutical industry, the water is used according to the US pharmacopoeia (USP) and European pharmacopoeia (EP) (ISPE, 2011). For the production of PW with the quality determined by the EP, enormous amounts of energy and water are expended. On the grounds of a decrease in water resources and an increase in consumption, a sustainable production system must be established for the production of needed water by consuming less energy (Xianli et al., 2014). According to EP, the maximum conductivity of PW at 20°C must be less than 4.3 μS/cm.

The flow diagram of the PW investigated in this study is depicted in Figure 1. The plant is composed of three main units: the first unit is the feeding and preliminary preparation process, consisting of an UF unit, raw water tank, and pump and activated carbon column; the second unit includes ion exchange columns for softening of the water and tank; a cartouche filter with a pore diameter of 5 m; an intermediate tank, reverse osmose membranes and pump; degasification membranes; an electrolyse unit; and UV lamb. The last unit of the plant is the deionised water storage tank and the distribution system, consisting of main and auxiliary deionised water storage tanks, distribution pumps, UV lamb, and heat exchanger.

Figure 1 Schematic of the WPU production plant



In the PW plant, the standard deviations of the measurements of the conductivity (μS/cm), pressure (bar), temperature (°C), and mass flow rate (kg/h) were 1%, 0.2%, ± 1, and 1%, respectively. These values were supported by the supplier and originally certified to the user when the system was installed. In addition, the factory's calibration team checks and makes sure these measurements are correct at a certain time.

3 The simulation study

For simulation of the desalination plant, the simulator software (COCO simulator) was used. The data used in the simulator was taken from the plant's operations in the summer season. The plant was analysed with the following assumptions:

- The treatment units of the plant were operating steadily.
- The salinity of the tap water was constant. The raw tap water was assumed to be an ideal solution of soluble electrolyte in water. The concentrations of all salt types in

the water were determined in terms of NaCl, which provides observation of salinity by conductivity, owing to ensure simplicity for simulation and calculation.

- The reference environment was assumed to be at 1 atm and 25°C.
- Because there were very few chemical reactions in the plant, the simulation software didn't include any chemical reactions at all.

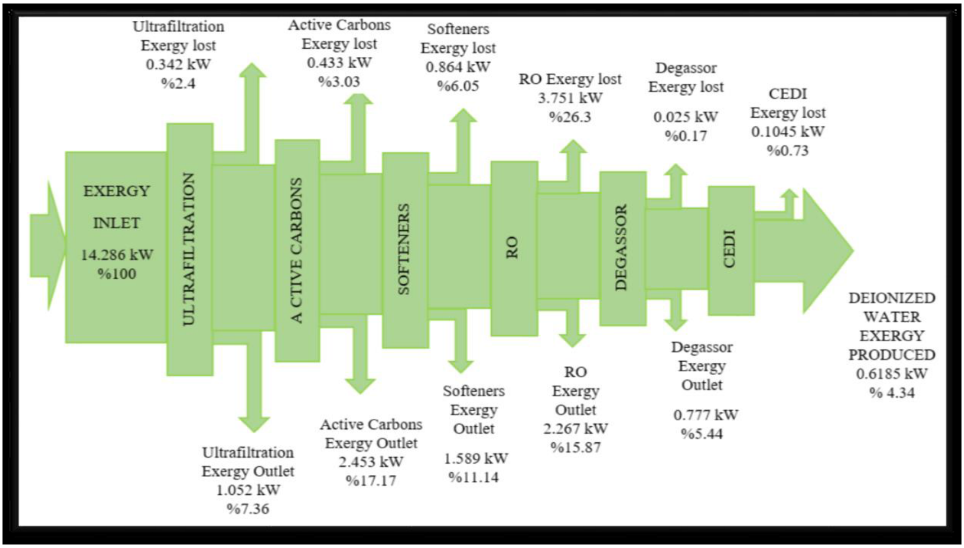
4 Results and discussion

The exergetic efficiencies and the exergy destruction of the plant are given in Table 1.

Table 1 The desalination plant exergy rate results

Treatment unit	*Exergy input rate (kW)*	*Exergy output rate (kW)*	*Destruction (kW)*	*Efficiency (%)*
UF	1.394	1.052	0.342	75.47
Activated carbon column	2.896	2.453	0.443	84.70
Softener columns	2.453	1.589	0.864	64.78
RO	6.018	2.267	3.751	37.67
Degasor	0.802	0.777	0.025	96.88
CEDI	0.723	0.6185	0.1045	85.50

Figure 2 Grassmann diagram for the operation during the summer season (see online version for colours)



As can be seen in Table 1 and the exergy band (Grassmann) diagram depicted in Figure 2 in the PW plant Figure 1, the process with the least exergetic efficiency was RO, the input exergy of which rate was 6.018 kW despite an output exergy of (0.802 + 1.465) kW, resulting in a destroyed exergy of 3,751 kW. This destruction accounted for 67.84%

of total energy destruction. The reason for the destruction stemmed from the inherent danger of RO. Osmosis is the spontaneous passage of a liquid from a dilute to a concentrated solution across a semi-permeable membrane, allowing the passage of the only solvent. The main reason for the movement of the liquid is to equalise the concentrations of the liquids on both sides of the membrane. The passage of solvent carries on where the pressure on the concentrated solution is high enough to preclude net passage of the solvent across the membrane. But, when any pressure greater than the osmotic pressure is applied on the more concentrated solution side of the membrane, solvent transfers from the side of the concentrated solution to the side of the less concentrated one. Therefore, in this plant, the pumps provided a high pressure of 1,780 kPa and the fluid friction that occurred throughout the membranes during filtration led to this high energy destruction. The softener column (ions exchange columns) was the second treatment unit in terms of energy destruction ratio, with 15.63% Table 1 in the PW plant given in Figure 1. Of all the ion exchange systems, the fixed-bed columns are the most preferred. The popularity of this technique is mainly due to its reduced labour cost. Softening may be achieved by using a strong acid cation exchanger to exchange Ca^{2+}, Mg^{2+}, and other divalent or polyvalent metallic ions, giving hardness to water by Na^+ ions through fixed-bed ion exchange columns at an operating pressure of 380 kPa. On the ground of their requirement for operating pressure and the decrease in conductivity of effluent, the softener column produced an output energy of 1,589 kW.

Given the energy destruction rate, the third process was the activated carbon column in the plant depicted in Figure 1. Their input and output exergy rates were 2,896 kW and 2,453 kW, respectively, resulting in an exergy destruction ratio of 8.01% Table 1. Activated carbon is widely used in water treatment to remove compounds that cause objectionable taste, odour, or colour. It is usually applied in granular form in the batch column, which is classified as fixed bed, counter-current bed, and fluidised-bed operations. However, the fixed-bed column used in this plant is the most widely used. In this PW, an activated carbon column was used to remove soluble organic matter turbidity, especially free chlorine and chloramines. Like softener columns, they were operated under a pressure of 360 kPa. Because of operation under lower pressure and lower removal of ion concentration compared to softener columns, the energy destruction of activated carbon was lower than that of softener columns.

Considering the energy loss ratio Table 1, the activated columns were followed by the UF unit with an energy loss of 6.29%, resulting from that exergy of 0.342 kW destroyed during UF due to operating pressure of 400 kPa. UF is referred to as a low-pressure membrane filtration process with a membrane pore diameter range of 10 A to 1,000 A, which can remove contaminants from drinking water with low capital and operating costs compared to nanofiltration and RO (Davey and Schafer, 2009; Gao et al., 2011). When the water filters through the filter under a trans-membrane pressure provided by a pump, the bacteria and most viruses are removed, and the water-related diseases can be prevented.

The CEDI unit that was used to remove ions from the effluent of RO was operated by applying electrical voltage to two carbon electrodes between which there are anion and cation exchange membranes. In the PW plant depicted in Figure 1, the energy destruction rate caused by CEDI was 0.1045 kW, corresponding to 1.89% of total energy destruction. On application of direct current to the electrodes, all cations begin to migrate toward the cathode. Also, all anions begin to migrate toward the anode. The cations can pass through the cation-permeable membrane, but they are obstructed from passing through the anion-permeable membranes. Similarly, anions can pass through the anion-permeable membranes but are obstructed from passing through the cation-permeable membranes.

In the PW, the least energy loss was determined in the degasser membrane, the aim of which was to strip soluble gases such as CO_2 from the effluent of RO to prevent corrosive effects in the subsequent units. The exergy degasser membrane rate and ratio in the total exergy loss of the degasser membrane were 0.025 kW and 0.44%, respectively Table 1.

As can be seen in the Grassmann diagram (Figure 2), the exergetic efficiency of this PW was determined as 4.35% Table 1. It means that this desalination process at specified rates could be implemented by only 0.6185 kW of energy instead of 1,052.34 kW. In the literature, any study investigating exergy analysis of PW plants operated for the pharmaceutical industry could not be found. But, compared to the study that produced tap water from brackish water by a desalination plant with an energetic efficiency of 8%, composed of NF, RO, and EDR (Kahraman et al., 2004), this efficiency is low. However, in a study, the aim of which was to produce potable water from saltwater by using RO, exergetic efficiency was calculated as 4.1%, around the energy efficiency of this study (Aljundi, 2009).

5 Conclusions

An analysis of the PW plant in the pharmaceutical industry was carried out. At the end of this study, the energy efficiency of the PW plant composed of the UF process, activated carbon column, softener columns, RO, degasser, and CEDI process was found to be 4.35%, which is low compared to modern power plants having an efficiency of over 50%. Therefore, significant opportunities are available to increase the energy efficiency of this desalination plant. By considering that most of the energy destruction in this plant stems from pump motors, especially one of RO, energy recovery devices such as pressure ex-changers and Pelton wheels may be used to increase the energy efficiency of the plant.

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Nomenclature

CEDI	Continuous electro deionisation unit
CGMP	Current good manufacturing practice
e	Specific exergy, J/kg
EP	European pharmacopoeia
EQ	Exergy of heat, W
ERD	Energy recovery devices
f	Process factor
g	Gravitational acceleration, m/s^2
h	Specific enthalpy, J/kg
I	Irreversibility rate, W
M	Mean molecular weight
m	Mass flow rate of a stream, kg/s
M	Molality
P	Proximity parameter
q	Activity
Q_h	Heat transfer rate, W
R	Rank order parameter
RO	Reverse osmosis
s	Specific entropy, J/kgK
T	Temperature, K
UF	Ultrafiltration
USP	United States pharmacopoeia
v	Mean flow velocity of a stream of substance, m/s
W	Input rate of useful work to the system, W
w	Weight
WPU	Water for pharmaceutical use
x	Molar fraction
z	Height above sea level, m
Greek letters	
η	Cumulative degree of performance
$\varnothing$	Exergetic efficiency
γ	Activity coefficient
Subscripts	
ch	Chemical
f	Fuel
h	Heat source
m	Molal
o	Value at environmental conditions
p	Product or by-product
r	Reactant or raw material (fuel not included)