Exergetic analysis of the chitosan-based treatment process for removing polycyclic aromatic hydrocarbons from seawater and sediments

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Abstract

The Bay of Cartagena (Colombia) is a site of commercial interest owing to its privileged location for maritime operations; however, the discharge of wastewaters from industrial activities and domestic sewage are affecting the water quality, and consequently, the biodiversity of coastal ecosystems. The polycyclic aromatic hydrocarbons (PAHs) are found in sediments and water of main ports, causing severe damage to the ecosystem. Thus, alternatives for the treatment of the Bay of Cartagena's water and sediments are needed. In this paper, we performed the exergetic analysis of removing PAHs from water and sediments in the Bay of Cartagena using an adsorption-based treatment process with chitosan microbeads and magnetic nanoparticles (CM-TiO$_2$/Fe$_3$O$_4$). The outcomes of exergy of utilities, irreversibilities and exergy losses were calculated using process data and exergy of substances. The Aspen plus V10 software provided the physical exergies, while chemical exergies were gathered from the literature. Overall exergy efficiency of 0.3% was determined for the seawater and sediment treatment facility. A sensitivity analysis was performed to identify the impact and viability of different design alternatives.

Key words: *efficiency, exergy, polycyclic aromatic hydrocarbons (PAHs), sensitivity analysis*

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a group of over 100 compounds formed by the fusion of two or more benzene rings, which replace carbon and hydrogen atoms [HUMEL *et al*. 2020]. They are considered an important class of Persistent Organic Pollutants (POPs) owing to their persistence to degradation, bioaccumulation into the environment, and toxicity to human health and ecosystems [MERAMO-HURTADO *et al*. 2020]. PAHs are target pollutants to monitor as they have mutagenic and carcinogenic properties [QIAO *et al*. 2019], which has motivated the issuing of environmental legislations including 16 PAHs of priority control [OLIVA *et al*. 2020].

The Bay of Cartagena, located in North-Colombia, is one of the bodies of water most affected in the city [MERAMO-HURTADO *et al*. 2018]. Even, it has been declared an environmental emergency in past years owing to the level of pollution. Several reasons are attributed to the presence of heavy metals, organic matter, and PAHs into this aquatic ecosystem. A recent diagnostic of seawater and sediments in the Bay showed a close relationship between the high levels of contamination, the toxicological level of fishes, and the public health of vulnerable communities in the coastal zone [El Tiempo 2018]. The domestic sewage from the population without access to sewerage system contributed significantly to total coliforms per day. Other research has shown the impact of hydrocarbons and pesticides on marine organisms in the bay, which could be expected considering the large amount of agriculture in the Magdalena basin and transportation activities [RESTREPO 2018]. The presence of hydrocarbons is attributed to the discharge of wastewater and persistent chemicals by industries that do not comply with environmental legislation [TOUS HERAZO *et al*. 2015]. The cleaning of pier and cargo ships is also a contributor to the levels of PAHs in many

zones of the bay [Caracol Radio 2019]. JOHNSON-RES-TREPO et al. [2008] compared the composition of PAHs in sediments from Cartagena Bay, Totumo Marsh, and Caimanera Marsh. They reported an average concentration of PAHs at 2090 ng·g^{-1} dry wt. for Cartagena Bay, which was around 8–12 times higher than Totumo and Caimanera.

Several physical and chemical technologies are tested at lab-scale to remove PAHs from aqueous environments [HUANG et al. 2016]. Among these, adsorption shows high removal efficiencies using materials such as biopolymers, activated carbon, and nanocomposites [GARCÍA-PADILLA et al. 2020]. Chitosan has been studied as an adsorbent to uptake hydrocarbons and other pollutants like dyes and heavy metals [GU et al. 2019]. This natural polymer derives from chitin, a substance found in the exoskeleton of crustaceans and fungal cell walls [MERAMO-HURTADO et al. 2019a]. Chitosan has good adsorption properties for the removal of hydrocarbons, along with flocculating ability and polyelectrolisity [PITAKPOOLSIL, HUNSOM 2014]. The presence of hydroxyl groups in chitosan chains contributes to its high adsorption efficiencies since they generate van der Waals interactions and hydrogen bonding with aromatic molecules in water-soluble hydrocarbons [FLORES-CHAPARRO et al. 2018]. Recent works also modify the chitosan matrix with nanoparticles to enhance its adsorption performance. They confer special properties to the adsorbent such as large surface area, biocompatibility and small particle size [SAINI et al. 2020].

In this work, a PAHs treatment system for seawater and sediments remediation was analysed from an exergy point of view. This analysis allows the identification of improvement opportunities through estimating exergy inefficiencies. The mapping of exergy losses will provide the stages that require design changes in terms of waste generation and utility consumption. This contribution is an extension of the work previously published [MERAMO-HURTADO et al. 2020] aiming to assess the performance of an adsorption-based treatment process to remove PAHs over the pillars of sustainability.

METHODS

PROCESS DESCRIPTION OF THE SYSTEM

The treatment of seawater and sediment containing PAHs is divided into four main sections: sedimentation (section I), adsorption (section II), recovery (section III) and desorption (section IV). In the first section, sediments are separated from the water for further PAHs removal using different technologies. The seawater stream is sent to the adsorption process using chitosan microbeads chemically modified with magnetic nanoparticles (CM-TiO$_2$/Fe$_3$O$_4$), which have shown removal yields up to 88% at lab-scale. The recovery of this adsorbent is addressed in section IV using hexane/acetone and magnetic separation. In this context, the solubility of PAHs in an organic solvent is exploited to drag them with the outlet hexane/acetone mixture. Then, this pollutant is separated from the solvents by boiling point difference. A magnetic field is implemented to take advantage of the magnetic properties of the adsorbent for PAHs desorption. The sediment stream feeds into section III, which includes three main stages: mixing, sedimentation and solvent recovery. The hexane/acetone mixture is also used as an organic solvent to drag the PAHs from the sediments. During sedimentation, the treated sediments leave the system and the PAHs-solvents mixture is sent to the solvent recovery stage [MERAMO-HURTADO et al. 2020].

EXERGETIC ANALYSIS

An exergetic analysis is a technique based on the laws of thermodynamics, which allows evaluating thermodynamic processes through the identification of the irreversibilities source, and consequently, inefficiencies in energy use [BOBBO et al. 2019]. This analysis determines the location, type, and real magnitude of the loss of energy resources. It has the advantage of calculating both the efficiency per stage and the overall efficiency of the process,
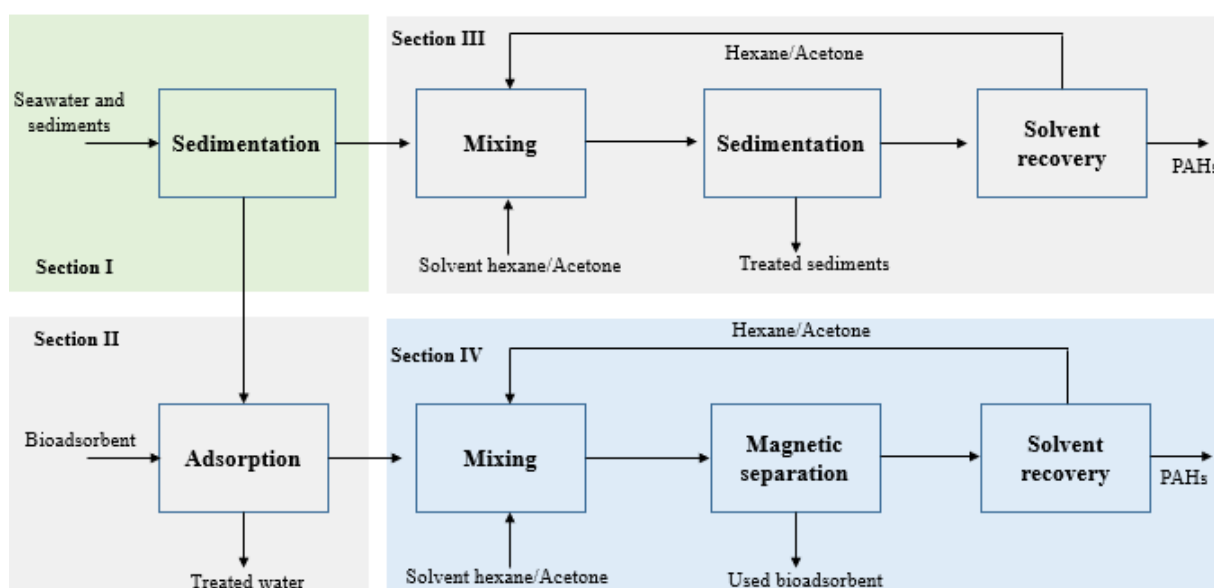

Fig. 1. Block diagram of the seawater and sediments treatment system; source: own elaboration

and helping to evaluate alternatives that increase energy efficiency and minimize energy losses [MARTINEZ *et al.* 2020; MORENO-SADER *et al.* 2019].

Equation (1) is used for the steady-state exergy balance. It relates the destroyed exergy ($Ex_{\text{des.}}$) to the net exergies by mass (Ex_{mass}), heat (Ex_{heat}), and work (Ex_{work}).

$$Ex_{\text{des.}} = Ex_{\text{mass}} + Ex_{\text{heat}} + Ex_{\text{work}} \qquad (1)$$

The transfer of exergy by work given in Equation (2) is directly proportional to the work done by the system when there is no change in volume.

$$Ex_{\text{work}} = W \qquad (2)$$

The exergy by heat transfer is associated with the temperature of the system and is calculated as follows:

$$Ex_{\text{heat}} = \sum \left(1 - \frac{T_0}{T}\right) Q_i \qquad (3)$$

The exergy transfer by mass flow is calculated using Equation (4); however, the potential exergy ($Ex_{\text{pot.}}$) and chemical exergy ($Ex_{\text{ch.}}$) tend to be negligible in the real process.

$$Ex_{\text{mass}} = Ex_{\text{ph.}} + Ex_{\text{ch.}} + Ex_{\text{pot.}} + Ex_{\text{k.}} \qquad (4)$$

Physical exergy ($Ex_{\text{ph.}}$) is the work that can be obtained by subjecting a substance to physical and reversible processes from the initial temperature and pressure to the state determined by the environment, as follows:

$$Ex_{\text{ph.}} = (H - H_0) - T_0(S - S_0) \qquad (5)$$

Where: H = system enthalpy, H_0 = enthalpy at environmental conditions, T_0 = environmental temperature, S = system entropy, S_0 = entropy at environmental conditions.

For gaseous substances, the calculation of physical exergy is given by Equation (6), assuming a constant heating capacity.

$$Ex_{\text{ph.}} = C_p(T - T_0) - T_0 \left(C_p \ln\frac{T}{T_0} - R\ln\frac{P}{P_0}\right) \qquad (6)$$

Where: C_p = heat capacity, R = universal gas constant, P = system pressure, P_0 = Environmental pressure.

For solid or liquid substances, the physical exergy is determined as follows:

$$Ex_{\text{ph.}} = C_p \left[(T - T_0) - T_0 \ln\frac{T}{T_0}\right] - v(P - P_0) \qquad (7)$$

Where: v = volume of substance.

The process involves a mixture of polar and non-polar substances; therefore, the mathematical model of Peng–Robinson was used to perform calculations of physical exergies in the Aspen Plus software.

Chemical exergy is the work that can be obtained from a substance under environment conditions if a state of thermodynamic equilibrium is reached through chemical reactions. For a mixture, this exergy ($Ex_{\text{ch.-mix}}$) is calculated as follows:

$$Ex_{\text{ch.-mix}} = \sum_i y_i \cdot Ex_{\text{ch.-}i} + RT_0 \sum_i y_i \cdot \ln(y_i) \qquad (8)$$

Where: y = mole fraction, i = component.

The calculation of the total exergy entering ($Ex_{\text{total-in}}$) a system is associated with the total inlet mass ($Ex_{\text{mass-in}}$) flows and utilities ($Ex_{\text{utilities-in}}$).

$$Ex_{\text{total-in}} = \sum Ex_{\text{mass-in}} + \sum Ex_{\text{utilities-in}} \qquad (9)$$

The calculation of the total exergy leaving ($Ex_{\text{total-out}}$) a system is associated with the outlet mass flow as products ($Ex_{\text{products-out}}$) and residues ($Ex_{\text{residues-out}}$).

$$Ex_{\text{total-out}} = \sum Ex_{\text{products-out}} + \sum Ex_{\text{residues-out}} \qquad (10)$$

The total exergy destroyed represents the irreversibilities of the process, i.e., the unused potential of the system to produce work. The exergy destroyed is proportional to the entropy generated in a process and is given by Equation (11).

$$Ex_{\text{des.}} = \sum Ex_{\text{total-in}} - \sum Ex_{\text{products-out}} \qquad (11)$$

The irreversibilities are classified into two groups: avoidable and non-avoidable. The first one corresponds to the exergy lost through waste streams that could be avoided if used. The latter is the lost exergy irreversibilities that derive from the increase in the entropy of thermodynamic systems.

$$Ex_{\text{loss}} = \sum Ex_{\text{total-in}} - \sum Ex_{\text{total-out}} \qquad (12)$$

The exergy efficiency is given by the Equation (13).

$$\eta_{\text{Ex.}} = 1 - \left(\frac{Ex_{des.}}{Ex_{\text{total-des.}}}\right) \qquad (13)$$

The percentage of exergy destroyed is given by Equation (14).

$$\%Ex_{\text{destroyed},i} = \left(\frac{Ex_{des.,i}}{Ex_{\text{total-des.}}}\right) \qquad (14)$$

A sensitivity analysis was also performed to determine the effect of adsorbent recirculation and operating conditions of equipment (evaporator) in the exergetic efficiency.

RESULTS AND DISCUSSION

EXERGY ANALYSIS

The exergy analysis required the calculation of chemical and physical exergy of streams involved in the process. The physical exergy was gathered from the simulation software Aspen Plus, while the chemical exergy was calculated using the equations previously described. Table 1 summarizes the chemical exergy of the compounds handled in the treatment of seawater and sediments.

As shown in Figure 2, the desorption unit reached the lowest exergetic efficiency per stage. When operating with seawater and sediments, the desorption stage has no output products; the output exergy takes a value of zero, making the irreversibilities equal to the input exergy. The highest value of irreversibilities is found in the recovery stage due to the heat that must be supplied to the evaporator, generating an increase in the input exergy value. The exergy of residues reported low values owing to the small waste generation within the process; however, the stream containing

Table 1. Chemical exergy of the compounds

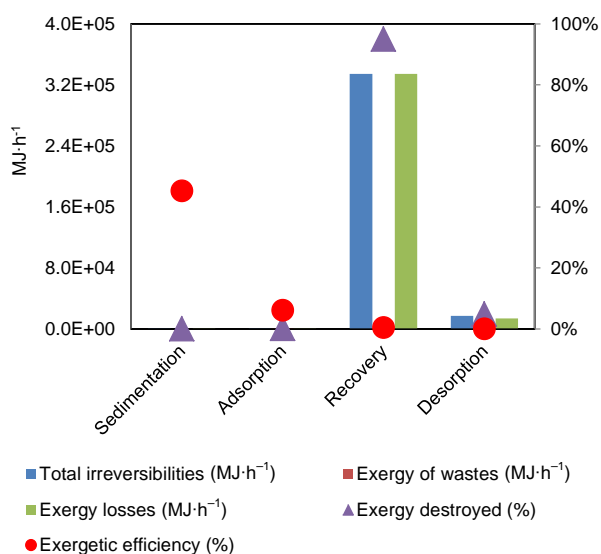| Compound	Chemical exergy (kJ·kg^{-1})
Water	42.75
SiO$_2$	36.62
CaCO$_4$	179.06
NaCl	251.19
NAPHT-01	41,368.31
CHITO-01	38,668.26
TiO$_2$	263.81
MAGNET	530.54
ACETO-01	30,764.42
N-HEX-01	47,740.98

Source: own study.

Fig. 2. Total irreversibilities, residue exergy, exergy losses, and exergy destroyed from a seawater and sediment chitosan treatment process; source: own study
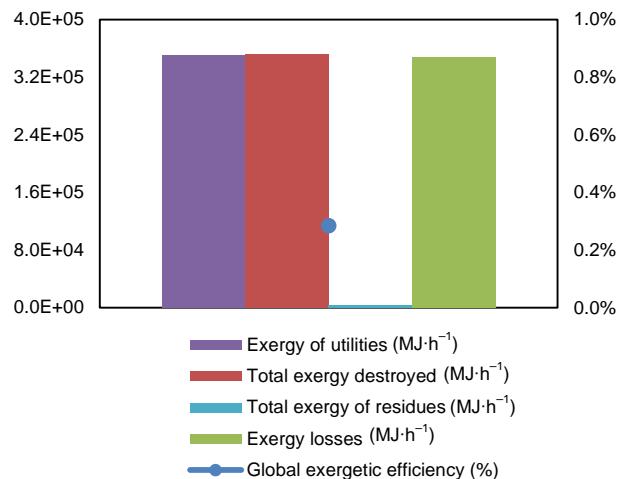

Fig. 3. Global exergy efficiency, exergy of utilities, total exergy destroyed, total exergy of residues, and exergy losses from a chitosan-based treatment process of seawater and sediments; source: own study

chitosan microbeads after PAHs desorption could be recycled to the adsorption stage. The recovery stage reached the highest exergy losses, followed by the desorption. Both stages were also responsible for the total irreversibilities and exergy destroyed.

The overall efficiency of the system was calculated at 0.3% due to the closeness between the total exergy destroyed (348,679.95 MJ·h^{-1}) and the total exergy input (349,652.58 MJ·h^{-1}). This low exergy efficiency is also observed for other emerging processes such as TiO$_2$ nanoparticles production [MERAMO-HURTADO *et al*. 2019b]. The heat required by the recovery stage evaporator (640,000 kJ·h^{-1}), and the desorption stage evaporator (32,000 kJ·h^{-1}), generate a significant contribution to the value of exergy by services. This process has a technical efficiency of more than 90% due to the low generation of wastes, which is reflected by the estimation of total exergy of wastes at 3,525.09 MJ·h^{-1} (see Fig. 3). Results also revealed similar values for total input exergy and total irreversibilities. As previously stated, the significant contribution to the irreversibilities comes from the recovery stage because the product outputs are minimal compared to the mass input. Furthermore, the mass input exergy is considerably low, and its contribution to the total input exergy is negligible compared to the contribution of the utility exergy, which is mostly due to the heat supplied to the evaporator in the recovery stage. From an energetic point of view, the removal of PAHs from seawater and sediments using the designed process needs several improvements. Any decrease of exergy losses will contribute to increasing the overall performance, leading to a more promising process for decision-makers.

Figure 4 shows a Sankey diagram representing the exergy losses by stages within the chitosan-based treatment process removing polycyclic aromatic hydrocarbons. The highest value of exergy destroyed corresponds to recovery, i.e., it is the stage where the most significant potential for producing work was not used, and the irreversibilities are unavoidable. Such stage reached the highest percentage of exergy destroyed at 95.02%, followed by the desorption stage at 4.85%. The percentages for sedimentation and adsorption are below 1%. This is the lowest amount of exergy destroyed from the process.
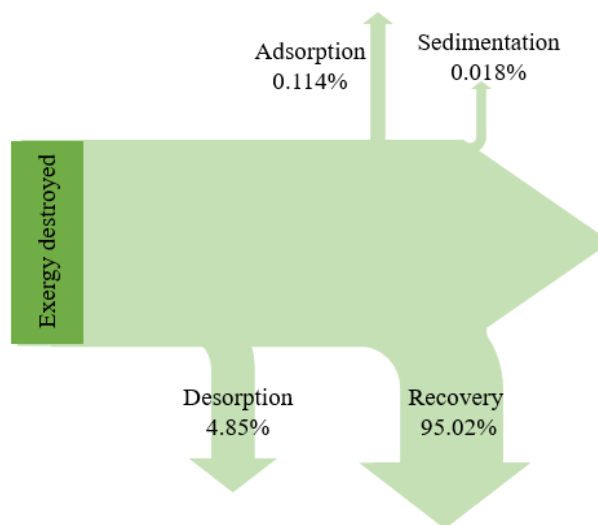

Fig. 4. Sankey diagram of exergy destroyed in the process; source: own study

SENSITIVITY ANALYSIS

In the sensitivity analysis, different scenarios are presented to show the influence of process variables on the overall exergetic efficiency. The first scenario is the recycling of the adsorbent after PAHs desorption in section IV. Figure 5 shows the change in process efficiency for this scenario. The global exergy efficiency increased up to 1.6 when implementing the design modification; however, an economic analysis must be conducted to determine any affectation to the project profitability by evaluating the cost of the equipment needed for the separation of nanoparticles from PAHs.
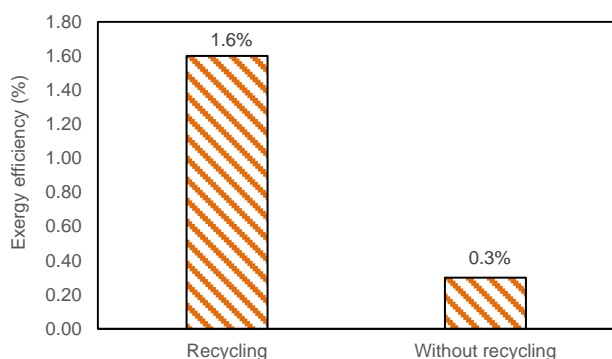

Fig. 5. Comparison of exergy efficiency when recirculating adsorbent; source: own study

Figure 6 shows the effect of temperature variation on the exergetic efficiency of the evaporators. The temperature variation was set in a range between 327.15 K and 332.15 K. For practical purposes, the pressure value was set at 84.09 kPa. As depicted in this figure, the efficiency of the evaporator decreases as temperature increases, revealing process sensitivity to operating conditions for such equipment. The highest efficiency (0.00162%) was observed at 327 K; however, the optimum value for the temperature is 331.15 K following recommendations found in the open literature, at which the efficiency reaches 0.000152%.
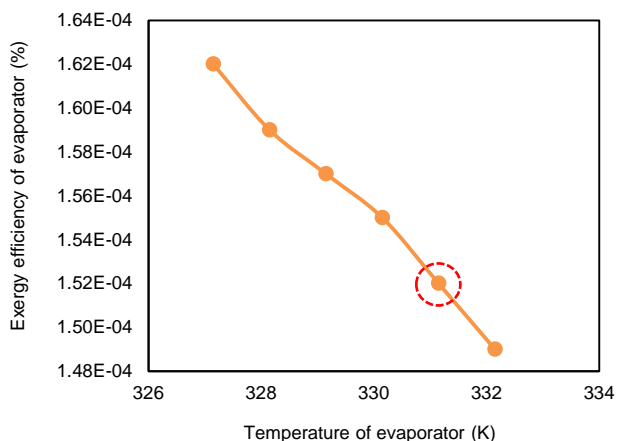

Fig. 6. Effect of evaporator temperature over the exergetic efficiency; source: own study

CONCLUSIONS

The chitosan-based treatment process removing polycyclic aromatic hydrocarbons (PAHs) from seawater has a low exergetic efficiency value (0.3%). However, based on the literature, this value is within the acceptable range for the exergetic efficiency of this type of process. The values of the physical exergies are close to zero because the operating conditions of the equipment are near the values of temperature and pressure reference. The overall efficiency of the process is lower compared to other water treatments, whose efficiency is around 60-70%. The low efficiency is mainly due to the significant contribution that the recovery process makes to the irreversibilities of the process. The sensitivity analysis made it possible to present specific appreciations about the process. It is the case of making a treatment to the stream 25 to recirculate the chitosan microbeads since this improves the efficiency considerably concerning the original process. Temperature fluctuation in the evaporator is not a significant factor in equipment efficiency variation. However, it is for the flow of the solvent since it is sensible to the range of temperatures, and the maximum rate of vapours is reached at a temperature of 331.15 K.

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