ABSTRACT: The presence of marine pollution in Cartagena Bay (Colombia) is an alarming environmental issue because of the ecotoxicological properties of contaminants such as polycyclic aromatic hydrocarbons (PAHs) that may affect the biodiversity of coastal ecosystems. In this sense, there is a need to propose alternatives to remediate the environmental pollution of such bodies of water. The aim of this work was to design an adsorption-based treatment process for the removal of PAHs from seawater and sediments. Two design cases were considered: (i) a base process without a PAH desorption unit and (ii) an alternative process including a PAH desorption unit. Both designs were simulated using Aspen Plus to obtain mass and energy balances. A parametric sensitivity analysis was carried out to determine optimum operating conditions for solvent recovery and treatment efficiency. The pressure and temperature of evaporators were selected as key parameters, as well as PAH loads in the influent. The environmental performance of base and alternative designs was also evaluated via waste reduction algorithm (WAR) methodology. A maximum recovered solvent flow rate was found when the evaporator operates at 56 °C and 0.81–0.83 atm. In addition, the total generation rate of potential environmental impacts (PEI) reported negative values for cases 1, 3, and 4 (−9.80 × 10⁻¹, −9.25 × 10⁺¹, −1.19 × 10⁻¹, and 1.04 × 10⁺¹ PEI/h). The major concern derived from this analysis is the high environmental impacts reached by the photochemical oxidation potential (PCOP) category associated with the use of hexane and acetone as solvents during PAH removal from sediments. In general, both designs of seawater and sediment treatment seem to be an environmentally friendly alternative for marine pollution remediation.

1. INTRODUCTION

The continuous deterioration of coastal waters due to pollution is an alarming fact that affects the functioning of aquatic ecosystems and biodiversity worldwide.¹ In North Colombia, Cartagena Bay is exposed to different contaminants coming from Canal del Dique, the industrial area of Mamonal, and a sewer system, which have contributed to human health and environmental concerns.² One of the major groups of pollutants that have been widely detected in such an aquatic ecosystem (as well as lakes, rivers, and wetlands) is polycyclic aromatic hydrocarbons (PAHs).³ They comprise a group of hydrophobic compounds consisting of two or more condensed aromatic rings and are included in the EU list of priority hazardous substances in surface waters.⁴,⁵ The presence of PAHs in coastal waters is derived from crude oil or refined petroleum products that are introduced into aquatic ecosystems from municipal wastewater in urban areas, incomplete combustion, spillage of fossil fuel, and vehicle exhaust.⁶ Besides, they can be found in marine sediments that can act as a secondary source of PAHs released into the surrounding environment.⁷ The major environmental concerns related to these pollutants are associated with their

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bioaccumulation and ecotoxicological properties that can cause different health problems such as cancer, endocrine disruption, abnormalities in the reproductive system, developmental disorders, and premature birth. 

According to the 2030 agenda for sustainable development, there is a need to prevent and reduce marine pollution in order to achieve a sustainable future.6 This need motivates the search for environmental remediation alternatives that eliminate or reduce the presence of contaminants like PAHs. In this context, several contributions have emerged to study PAH removal at a lab scale using different adsorptive materials. For example, Wickramasinghe and Shukla6 evaluated the PAH uptake from aqueous solution employing a low-cost absorbent that was prepared from plaster of Paris, coconut coir, zeolite, chitosan, and algic acid. They reached high removal yields up to 91% that suggested promising applicability of this material to wastewater treatment. Another important work was performed by Ge et al.10 in which they used activated carbon coming from coal and iron to treat main constituents of PAH pollutants, and reported adsorption capacities of 160.88, 181.99, and 199.07 mg/g for naphthalene, phenanthrene, and pyrene, respectively. Other works have also focused on evaluating the adsorption of PAHs with materials based on nanotechnology, for example, Huang et al.11 synthesized magnetic nanoparticles containing a maghemite core and silica mesoporous layer (Mag-PCMA-T) and performed batch adsorption experiments to determine its sorption capacity. They achieved removal efficiency of PAHs above 85% in less than 30 min with relatively high sorption capacity (up to 1060 mg/kg).

Despite the efforts of the scientific community in developing highly efficient alternatives to face the loads of PAHs in wastewater and sewage, contamination of the aquatic environment persists, and some of the reasons are attributed to the following: (i) The removal efficiencies are less for real processing volume than for lab-scale conditions, (ii) the capital investments and operating costs of novel treatment technologies at a large scale are significantly high to be incorporated within a processing plant, and (iii) no information in the literature supports the feasibility of scaling up technologies first developed at a lab scale. In this sense, a knowledge gap was identified in the design, simulation, and assessment of integrated systems based on scaled-up technologies. These systems emerge due to the ineffectiveness of typical operations in water treatment plants for several pollutants’ removal like PAHs.12 They may refer to coupling additional stages such as adsorption using novel materials and its regeneration to conventional treatment plants. The main purpose of these integrated systems is not only to reduce biochemical oxygen demand (BOD) but also to remove toxic and carcinogenic substances in order to meet standard quality of water and not incur legal penalties.13,14

Table 1 summarizes relevant contributions found in the literature for several types of wastewater treatment plants. For example, Tian et al.15 developed a designing scheme to treat organic-rich wastewater using ester (2,2,4-trimethyl-1,3-pentanediol-diisobutyrate, TXIB) as an extractant. They also simulated the design of the wastewater process in Aspen Plus software and determined optimum parameters through experimentation. The simulation of the PAH wastewater treatment process was studied by Jing et al.16 using UV irradiation and advanced oxidation technologies. They investigated the degradation mechanism of PAHs, and the resulting experimental data was entered into an artificial neural network simulation model based on a dynamic mixed integer nonlinear programming approach. Other contributions performed environmental assessment of wastewater treatment processes using computer-aided tools such as life cycle assessment (LCA). To date, no research studies are found in the literature related to the simultaneous design, simulation, and environmental assessment of the PAH treatment process in seawater and sediments.

This work is focused on the design and simulation of a water treatment process for the removal of PAHs from seawater and sediments. In addition, parametric sensitivity analysis and environmental assessment are performed to evaluate the effect of operating variables on process performance as well as estimate the potential toxicological and atmospheric impacts. For the first time, chitosan microbeads modified with TiO2 and magnetite nanoparticles (CM-TiO2/Fe3O4) were incorporated as an adsorbent in the design and simulation of a large-scale treatment process for PAH removal in North Colombia. The main core of this research was to provide a suitable alternative to reduce marine pollution in Cartagena Bay by implementing an efficient and environmentally friendly process that includes a PAH adsorption process.

2. METHODOLOGY

The process system for PAH removal was designed according to the physicochemical properties of seawater and sediments in Cartagena Bay. The technology selected for PAH uptake was adsorption because of its high efficiency, low cost, and easy implementation.17 Chitosan microbeads modified with TiO2 and magnetite nanoparticles (CM-TiO2/Fe3O4) were employed as an adsorbent. The PAH removal yield of such microbeads was previously estimated by performing lab-scale batch adsorption experiments. For sediment treatment, the solvent extraction method suggested by the EPA was used.22 Figure 1 depicts a general representation of the main methodological steps followed in this work. As a first approach, a block diagram of the large-scale process was built in order to identify the main stages required for an efficient pollutant removal. The following design cases were considered:

(i) a base process without a PAH desorption unit and
(ii) an alternative process including a PAH desorption unit.

Then, both design cases were simulated with Aspen Plus software in order to obtain extended mass and energy balances.

| Table 1. Recent Contributions on the Design, Simulation, and Environmental Assessment of Several Treatment Processes |
|---|---|---|---|---|
| treatment processes | design | process simulation | environmental assessment | reference |
| organic wastewater treatment | x | x | Tian et al.15 |
| spent caustic wastewater treatment | x | Chandraaseagar et al.17 |
| spent caustic wastewater treatment | x | Almadi et al.16 |
| Budapest central wastewater treatment plant | x | Garsió et al.19 |
| marine oily (PAHs) wastewater treatment | x | Jing et al.16 |
| Cairo wastewater treatment plants | x | Al-Dosary et al.20 |
| PAH treatment process | x | x | this work |
The thermodynamic property package selection was based on the nature of the substance involved in the process. The effect of operating variables on process performance was assessed via parametric sensitivity analysis. The final methodology step was to evaluate the environmental impact of the design cases through the computer-aided tool waste reduction algorithm (WAR).

2.1. Process Design and Simulation. The treatment system is designed to be in Cartagena de Indias (North Colombia) with the aim of removing PAHs from contaminated water and sediments in Cartagena Bay, an important marine ecosystem. The authors previously performed monitoring in Cartagena Bay to determine physicochemical properties of superficial water and sediments. Such research work stated similar geographic conditions to those reported by Guigue et al., hence, both contributions were used to gather information about the influent. During design and simulation, the following assumptions were set:

(i) Process simulation was in a steady state because of the benefits that it can deliver for a better understanding of process behavior.
(ii) The PAHs were mainly composed of naphthalene as reported by Jing et al.
(iii) The grit separation efficiency was set in 90% according to the specification of suppliers for wastewater solutions and concepts of wastewater engineering.
(iv) An electrolyte non-random two-liquid model (electrolyte-NRTL) was used to model thermodynamic properties because it properly correlates equilibrium data for a variety of dilute salt/mixed solvent systems.
(v) The removal yield of CM-TiO2/Fe3O4 was set in 88% because it was the most promising result obtained in batch adsorption experiments at a lab scale.
(vi) The extraction method with a hexane/acetone mixture was selected for sediment remediations following previous works.
(vii) The solubility of naphthalene in the hexane/acetone mixture was modeled in an RSTOIC simulation block owing to the unknown kinetics of reactions that may take place when HAPs are diluted in nonpolar compounds.
(viii) Sediments in Cartagena Bay were modeled as a mixture of granular materials of sand, silt, and clay according to its composition previously reported in the literature.
(ix) Sand is modeled as a mixture of silicon oxide and calcium sulfate (main constituents).
(x) Despite the presence of several salt types, seawater was modeled using the sodium chloride compound (main constituent).

2.2. Parametric Sensitivity Analysis. After modeling the design cases, a parametric sensitivity analysis was performed to identify optimum operating conditions in critical sections that could affect the overall process performance. In Section 3, the recovery of solvent depends of the conditions under which the evaporator works and may influence the separation efficiency between PAHs and the hexane/acetone mixture. To assess the change of the recovered solvent flow rate, the temperature and pressure of the evaporator was varied in the simulated process for a range between 54 and 59 °C and 0.81 and 0.86 atm, respectively. The optimal selection of temperature and pressure leads to a higher solvent evaporation rate, i.e., higher recovery efficiency, and reductions in energy consumption. Another key process parameter is the composition of influent in terms of PAHs because of the decrease in treatment efficiency when increasing contaminant loads. In this sense, a sensitivity analysis was performed to evaluate the changes in final PAH content of treated seawater and sediments when varying PAH loads in the influent from 70 to 150% of the standard design value (0.037 kg/h).

2.3. Environmental Assessment. The methodology of computer-aided WAR algorithm was applied to evaluate the environmental performance of both design cases using the mass and energy balances provided by the simulation software. In order to identify the contributions of energy flow on environmental impacts, four different assessment cases were considered:

(i) (case 1) a base design without considering energy flow,
(ii) (case 2) a base design considering energy flow,
(iii) (case 3) an alternative design without considering energy flow, and
(iv) (case 4) an alternative design considering energy flow.

For all these cases, the contribution of product streams was included within the analysis. The WAR algorithm methodology was first introduced by the United States Environmental Protection Agency (EPA) for the design of sustainable processes. This tool allows us to quantify the rate of generation or consumption of potential environmental impacts within a chemical process. The impact categories included in WAR algorithm are global warming potential (GWP), ozone depletion potential (ODP), acidification potential (AP), photochemical oxidation potential (PCOP), human toxicity potential by ingestion (HTPI), human toxicity potential by exposure (HTEP), aquatic toxicity potential (ATP), and terrestrial toxicity potential (TTP). All these categories are divided into two main groups: toxicological categories and atmospheric categories. Table 2 summarizes the mathematical equations used to calculate such impact categories.

The terms \( a_i \) and \( a_{\text{CO}_2} \) are the radiation heat absorption per unit of greenhouse gas \( i \) and per unit of carbon dioxide; \( c_i(t) \) and \( c_{\text{CO}_2}(t) \) are the greenhouse gas \( i \) concentration and the carbon
The term $\text{[O}_3\text{]}$ removes the depletion of global ozone produced by chlorofluorocarbon CFC-11; $\alpha_i$ is the change in ozone concentration due to the change in a volatile organic compound emission; $b_i(t)$ and $b_{C_2H_4}(t)$ are the integrated emission of a volatile organic compound $i$ up to time $t$ and the integrated emission of ethylene at the same time. $V_i$ and $V_{SO_2}$ are the acidification potential of component $i$ and $SO_2$; $M_i$ and $M_{SO_2}$ are the mass unit of substance $i$ and $SO_2$.32

3. RESULTS AND DISCUSSION

3.1. Design of the Water Treatment Process. According to the assumptions stated in section 2.1, the water treatment process was designed for removing PAHs from both sediments and seawater. As shown in Figure 2a, the base design included three main sections: Section 1 is incorporated within the process to separate sediments from seawater; Section 2 refers to the adsorption unit using chitosan microbeads chemically modified with nanoparticles (CM-TiO$_2$/Fe$_3$O$_4$); Section 3 is a solvent extraction unit with a hexane/acetone mixture for sediment treatment. An additional section was considered in the alternative design to recover the adsorbents loaded with PAHs. Figure 2b shows the block diagram for the designed water treatment process including a PAH desorption unit. This design incorporated magnetic separation to take advantage of the magnetic properties of the selected biosorbents and remove the PAHs/nonpolar solvent mixture from the adsorptive materials.

3.2. Process Simulation of the Process. The water treatment process was simulated for a mass flow rate of 1000 kg/h of contaminated influent, i.e., seawater and sediments. The chemical composition of influent was reported by Meramo-Hurtado et al.23 and Guigue et al.24 Table 3 summarizes the main process data for the influent with PAH loads around $3.7 \times 10^{-5}$ g/g for both sediments and seawater. The operating conditions of the main process streams for base and alternative designs are found in the Appendix section.

Table 2. Impact Categories Included in WAR Algorithm

| category | toxicological categories | equation | parameters of reference |
|----------|--------------------------|----------|------------------------|
| HTPI     | $\text{HTPI} = \frac{1}{LD_{50}}$ | rat oral lethal dose ($LD_{50}$) |
| HTPE     | $\text{HTPE} = \frac{1}{TLV}$ | threshold limit values (TLV) |
| ATP      | $\text{ATP} = \frac{1}{LC_{50}}$ | lethal concentration ($LC_{50}$) |
| TTP      | $\text{TTP} = \frac{1}{LD_{50}}$ | rat oral lethal dose ($LD_{50}$) |

| category | atmospheric categories | equation | reference parameter |
|----------|------------------------|----------|---------------------|
| GWP      | $\text{GWP} = \int_a^{\text{CO}_2(t)} dt \int_{m_i}^{c_{\text{CO}_2}}$ | carbon dioxide emission ($c_{\text{CO}_2}$) |
| ODP      | $\text{ODP} = \int_0^{\text{[O}_3\text{]}(t)} dt \int_{a_i}^{d_{\text{O}_3}}$ | depletion of global ozone ($d_{\text{O}_3}$) |
| PCOP     | $\text{PCOP} = \int_{\text{C}_2\text{H}_4}^{\text{c}_{\text{C}_2\text{H}_4}} dt \int_{m_i}^{a_{\text{C}_2\text{H}_4}}$ | change in $C_2H_4$ emission ($a_{\text{C}_2\text{H}_4}$) |
| AP       | $\text{AP} = \frac{\text{V}_{SO_2}}{m_{SO_2}}$ | acidification potential for $SO_2$ ($V_{SO_2}$) |

Figure 2. Block diagram of the water treatment process: (a) base design and (b) alternative design.
Figure 3 depicts the process flow sheet of the base design for treating seawater and sediments contaminated with PAHs. The sedimentation section was simulated to separate sand from seawater using a grit chamber (GCHAMBER) and a settler (SEDIMENT). The chamber removes a large fraction of heavy sediments while the settler is employed to remove finer particles from water. Then, a mixer equipment (MIXINGSO) was selected to collect streams leaving both chamber and settler (streams 3 and 4, respectively). The resulting mixture was sent to a solvent extraction unit in order to remove PAH pollutants from sediments.35 In such a unit, sediments were contacted with solution of hexane and acetone through a mixer (SOLVENT) in order to develop chemical affinity interactions between solvent and PAHs. The solubility phenomenon of PAHs in the hexane/acetone mixture took place on an RSTOIC block. The stream leaving such a block is separated from sediments in a settler (SOLSEP). An evaporation stage (EVAPORAT) was incorporated to recover solvents (stream 15) from PAHs (stream 18). The solvent stream was cooled with a condenser (COND) and recycled into the process.36 The seawater leaving the sedimentation section was fed into an adsorption unit to separate pollutants from water. Such a unit employs chitosan microbeads modified with nanoparticles (CM-TiO2/Fe3O4) with a removal yield of 88% (stream 6). The treated water (stream 8) was sent back to the coastal ecosystem, i.e., Cartagena Bay. The base design was limited to PAH adsorption without adsorbent recovery, and hence, the chitosan microbeads loaded with PAHs were not subjected to further recovery stages.

Figure 4 shows the simulation diagram for the water treatment process coupled with a PAH desorption unit (magnetic separation). As chitosan microbeads were modified with magnetite nanoparticles (Fe3O4), the adsorbent material is attracted to magnetic fields. A solvent extraction procedure was also incorporated to improve desorption results. The adsorbent loaded with PAHs was mixed with nonpolar solvents hexane/acetone to reach the equilibrium for further phase separation using magnetic fields (MAGSEP). The phenomenon in which PAHs are dissolved in nonpolar substances was modeled as an RSTOIC block (SOLB2). The stream leaving magnetic separation equipment (stream 25) was fed into an evaporator (EVAP2) for removing PAHs from solvents owing to the difference of boiling points. The recovered solvents were recycled into the process, and the stream of PAHs was mixed with the PAHs removed from sediments in the solvent extraction unit.

### 3.3. Parametric Sensitivity Analysis

Figure 5a shows the effect of temperature on solvent recovery in Section 3. It was found that the system is highly sensitive to a temperature range of 54 to 56°C, and the flow rate of volatile solvent vapors leaving the evaporator stays constant after reaching 56°C. According to these results, the maximum solvent recovery was reached at 56°C suiting the optimum value for evaporator temperature. As shown in Figure 5b, the flow rate of hexane/acetone vapors reduces drastically from 1311.88 to 0 kg/h as the evaporator pressure increases. These results are explained by basic thermodynamic principles in standard thermally driven unit operations. The boiling point increases with increased pressure, and the set temperature is not high enough to reach this point; thus, vapor generation decreases.37 Based on the above analysis, the optimum pressure values are in the range of 0.81 to 0.83 atm.

Table 3. Main Process Data for the Influent Stream

| Component | Concentration (g/g) | Main Compounds | Mass Flow Rate (kg/h) |
|-----------|---------------------|----------------|----------------------|
| Water     | 0.62                | H2O            | 620.00               |
| Sand      | 0.38                | SiO2 + CaSO4   | 380.00               |
| Silt      | 0.26                | SiO2           | 262.20               |
| Clay      | 0.12                | CaSO4          | 117.80               |
| PAHs      | 3.7 × 10^-5        | naphthalene    | 0.014                |

| Component | Concentration (g/g) | Compounds | Mass Flow Rate (kg/h) |
|-----------|---------------------|-----------|----------------------|
| Water     | 0.97                | H2O       | 596.30               |
| Salt      | 0.04                | NaCl + CaSO4 | 21.70          |
| NaCl      | 0.03                | NaCl      | 19.68                |
| CaSO4     | 3.3 × 10^-3        | CaSO4     | 2.02                 |
| PAHs      | 3.7 × 10^-5        | naphthalene | 0.023               |

“Sand is composed of silt and clay. “Salts are composed of NaCl and CaSO4.

Figure 3. Simulation flow sheet of the base design.
efficiency of seawater and sediments. For a standard design value of PAH loads (0.037 kg/h), the final content of PAHs in treated seawater and sediments were $4.30 \times 10^{-6}$ and $7.17 \times 10^{-4}$ kg/h, respectively. When increasing the content of pollutants in the influent, a linear increase of the PAH flow rate was found in both treated streams; however, this operating parameter affected more the sediment treatment than seawater treatment. The concentration of PAHs on effluents reached values around $0.47-1.00$ μg/L for the interval of PAH loads. These concentrations are within the limit established by the national environmental policy concerning the discharges of residual water into bodies of water (resolution 0631/2015).

Figure 4. Simulation flow sheet of the alternative design.

Figure 5. Effect of evaporator conditions on generating solvent vapors: (a) temperature and (b) pressure.

Figure 6. Effect of PAH content in the influent on treatment process performance for (a) seawater and (b) sediments.

3.4. Environmental Assessment. Figure 7 shows a comparison of global generation of environmental impacts as well as output rates for all cases. The total generation rate of PEI reported negative values for cases 1, 3, and 4 ($-9.80 \times 10^{-3}$, $-9.25 \times 10^{1}$, $-1.19 \times 10^{2}$, and $1.04 \times 10^{2}$), suggesting an environmentally friendly performance of the designed treatment systems. These results were expected because both plants are designed to reduce the waste generation by recycling solvents within the process and use biodegradable materials for biosorbent synthesis such as chitosan. Despite case 2 generating environmental impacts, it was significantly low in comparison with other chemical processes. Higher PEI output and generation rates for the base design than the alternative.
design were found. The main reason for this result is that the alternative design includes further purification of adsorbents, reducing the product streams that impact the environment.

Similar values were reached for cases 1 and 2 as well as cases 3 and 4, suggesting that energy flows do not contribute to the environmental impacts of such processes.

Figure 8 depicts the toxicological environmental impacts per impact category (HTPE, HTPI, TTP, and ATP) for all four cases. The output rate of PEI is significantly high for the HTPE category compared with other toxicological categories. Such a result is attributed to the presence of PAHs in output streams, which are recognized as hazardous substances owing to its bioaccumulation and toxicological properties. The aquatic toxicity potential reported values of $4.82, 4.84 \times 10^{11}, 7.11,$ and $7.13 \times 10^{11}$ PEI/h for cases 1, 2, 3, and 4, respectively. As treated seawater and sediments will be sent back to the surface of bodies of water, the ATP category becomes a key aspect to consider during environmental assessment. The low values for the ATP category seem to be a promising finding because the streams leaving the treatment process do not represent any concern regarding contamination of the coastal ecosystem by toxic substances. The negative results in the total generation rate of PEI per category confirmed the good overall performance of the process from an environmental point of view.

Figure 9 depicts the environmental performance of both base and alternative designs regarding emissions into the atmosphere. The global categories (GWP and ODP) exhibited the lowest values of the generation and output rate of PEI, suggesting that substances involved within the process contributed less to global warming and ozone depletion. In fact, the output rate of PEI was zero under GWP, ODP, and AP categories for cases 1 and 3. The increase in the output rate of PEI for cases 2−4 compared with cases 1−3 revealed that energy sources contributed to atmospheric environmental impacts. The major concern derived from this analysis is the PCOP category because of the high values reached (8.14 and 8.57 PEI/h). These results are associated with the use of hexane and acetone as solvents during PAH removal from sediments. Moncada et al. stated that solvent extraction techniques using hexane generate severe impacts on photochemical oxidation potential. Despite efforts to reuse solvents, a solvent fraction that is not completely separated during evaporation is discharged into the environment along with sediments.

4. CONCLUSIONS
This work provided a novel design approach for the treatment of seawater and sediments contaminated with hazardous polycyclic aromatic hydrocarbons, which considered the use of chitosan microbeads modified with TiO$_2$ and magnetite nanoparticles previously synthesized at a lab scale by the authors. The application of novel materials such as nanotechnology-based biosorbents in an integrated treatment system at a large scale offered insights about the suitability of scaling up technologies in terms of efficiency and environmental performance. The environmental assessment via the WAR tool proved that both base and alternative designs were environmentally friendly because of the negative values for the total generation rate of PEI; however, the replacement of hexane and acetone with green solvents in the process Section 3 represents a future work to address. Finally, the design, simulation, and environmental evaluation of this treatment process reported meaningful information in the use of novel adsorptive materials as a remediation alternative for coastal ecosystem pollution.

5. FUTURE WORKS
The development of this work leads to the identification of future prospects such as:

(i) to perform a technical economic analysis for both design alternatives in order to select the most feasible process design,

(ii) to perform process safety assessment methodology to identify hazardous units within the designs,

(iii) to perform mathematical programming in order to optimize synthesis of the PAH removal process, and

(iv) to replace nonpolar solvents with green solvents to enhance environmental performance of the process.

A: APPENDIX
The operating conditions for process streams of the base and alternative design are shown in Tables A1 and A2.
Table A1. Main Process Streams for the Base Design

| Stream name | 1      | 5      | 6      | 7      | 8      | 9      |
|-------------|--------|--------|--------|--------|--------|--------|
| temperature (°C) | 30     | 30     | 28     | 29.9941| 29.9941| 30     |
| pressure (atm)   | 1.01972| 1.01972| 1.01972| 1.01972| 1.01972| 1.01972|
| mass flow rate (kg/h) | water 620 | 620 | 0 | 0 | 620 | 0 |
|                | SiO₂    | 262.2  | 0     | 0     | 0     | 262.2  |
|                | CaSO₄   | 119.82 | 2.02  | 0     | 0     | 2.02   |
|                | NaCl    | 19.68  | 19.68 | 0     | 0     | 19.68  |
|                | NAPHT-01| 0.037  | 0.023 | 0     | 0.023 | 0.014  |
|                | CHITO-01| 0      | 0     | 9.36  | 9.36  | 0      |
|                | TiO₂    | 0      | 0     | 4.68  | 4.68  | 0      |
|                | MAGNETIT| 0      | 0     | 4.68  | 4.68  | 0      |
|                | ACETO-01| 0      | 0     | 0     | 0     | 0      |
|                | N-HEX-01| 0      | 0     | 0     | 0     | 0      |
| total          | 1021.74 | 641.723| 18.72 | 18.743| 641.7  | 380.014|

| stream name | 10     | 11     | 16     | 17     | 18     | 19     |
|-------------|--------|--------|--------|--------|--------|--------|
| temperature (°C) | 28     | 28.1729| 58     | 28     | 28     | 28     |
| pressure (atm)   | 1.01972| 1.01972| 0.815773| 1.01972| 1.01972| 1.01972|
| mass flow rate (kg/h) | water 0 | 0 | 0 | 0 | 0 | 0 |
|                | SiO₂    | 0      | 262.2  | 13.11  | 0     | 13.11  |
|                | CaSO₄   | 0      | 117.8  | 5.89   | 0     | 5.89   |
|                | NaCl    | 0      | 0      | 0      | 0     | 0      |
|                | NAPHT-01| 0      | 0.014  | 0.01365| 0     | 0.01365|
|                | CHITO-01| 0      | 0      | 0      | 0     | 0      |
|                | TiO₂    | 0      | 0      | 0      | 0     | 0      |
|                | MAGNETIT| 0      | 0      | 0      | 0     | 0      |
|                | ACETO-01| 16.819 | 672.758| 0      | 655.939| 0      |
|                | N-HEX-01| 16.819 | 672.758| 0      | 655.939| 0      |
| total          | 33.638 | 1725.53| 19.0137| 1311.88| 19.0137| 1345.52|

**ADDITIONAL NOTE**

"The operating conditions are initial naphthalene concentration of 100 mg/L, room temperature of 30 °C, solution pH of 6, adsorbent dosage of 3 g/L, and contact time of 24 h.

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Table A2. Main Process Streams for the Alternative Design

| stream name | 1          | 2          | 5          | 7          | 9          | 10         |
|-------------|------------|------------|------------|------------|------------|------------|
| temperature (°C) | 30         | 30         | 30         | 29.9941    | 30         | 28         |
| pressure (atm)   | 1.01972    | 1.01972    | 1.01972    | 1.01972    | 1.01972    | 1.01972    |
| mass flow rate (kg/h) |            |            |            |            |            |            |
| water          | 620        | 620        | 620        | 0          | 0          | 0          |
| SiO₂          | 262.2      | 262.2      | 0          | 0          | 262.2      | 0          |
| CaSO₄         | 119.82     | 13.8       | 2.02       | 0          | 117.8      | 0          |
| NaCl          | 19.68      | 19.68      | 19.68      | 0          | 0          | 0          |
| NAPHT-01      | 0.037      | 0.0244     | 0.023      | 0.023      | 0.014      | 0          |
| CHITO-01      | 0          | 0          | 0          | 9.36       | 0          | 0          |
| TiO₂          | 0          | 0          | 0          | 4.68       | 0          | 0          |
| MAGNETIT      | 0          | 0          | 0          | 4.68       | 0          | 0          |
| ACETO-01      | 0          | 0          | 0          | 0          | 0          | 16.819     |
| N-HEX-01      | 0          | 0          | 0          | 0          | 0          | 16.819     |
| total         | 1021.74    | 679.724    | 641.723    | 18.743     | 380.014    | 33.638     |

| stream name | 16         | 19         | 21         | 25         | 28         | 29         |
|-------------|------------|------------|------------|------------|------------|------------|
| temperature (°C) | 58         | 28         | 55.0037    | 28         | 58         | 28         |
| pressure (atm)   | 0.815773   | 1.01972    | 0.826582   | 1.03323    | 0.826582   | 1.03323    |
| mass flow rate (kg/h) |            |            |            |            |            |            |
| water          | 0          | 0          | 0          | 0          | 0          | 0          |
| SiO₂          | 0.2622     | 0          | 0          | 0          | 0          | 0          |
| CaSO₄         | 0.1178     | 0          | 0          | 0          | 0          | 0          |
| NaCl          | 0          | 0          | 0          | 0          | 0          | 0          |
| NAPHT-01      | 0.01365    | 0          | 0          | 0.022425   | 0.022425   | 0.022425   |
| CHITO-01      | 0          | 0          | 0          | 0          | 0          | 0          |
| TiO₂          | 0          | 0          | 0          | 0          | 0          | 0          |
| MAGNETIT      | 0          | 0          | 0          | 0          | 0          | 0          |
| ACETO-01      | 0          | 0          | 0          | 0          | 0          | 16.819     |
| N-HEX-01      | 0          | 0          | 0          | 0          | 0          | 16.819     |
| total         | 0.39365    | 1345.52    | 66.6398    | 64.9962    | 0.022425   | 0.022425   |

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