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Computer aided environmental analysis of a large-scale production of chitosan micro-beads modified with thiourea and magnetite

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Abstract. In this work, environmental assessment of a large-scale production of chitosan micro-beads modified with thiourea and magnetite was performed using Waste Reduction Algorithm (WAR). This methodology evaluates eight impact categories, four toxicological and four atmospherics. Initially, the simulation of production process of micro-beads was realized. Then, WAR GUI software, which is based on WAR algorithm, was employed to quantify potential environmental impacts (PEI) generation and output rate for this process under 4 different cases. The synthesis of micro-beads was analysed using computer-aided process engineering, this is related to the fact that there is no bibliography reported for the industrial scale-up, simulation and environmental evaluation of this type of process Results shows that photochemical oxidation potential is the evaluated category which emits the biggest output rate of PEI, contributing in all cases with more than 49% of the total rate. In general terms, the process has a negative generated PEI which means that the process has a convenient environmental performance. This leads to the conclusion that the process is environmentally beneficial because it consumes environmental impacts.

1. Introduction

In recent years, water pollution by heavy metals, dyes, solids and hydrocarbons represents a serious threat to the environment and humans [1]. As a solution to this problem, several technologies have been proposed, where adsorption process becomes in an important alternative because its practical, economic and environmentally friendly methods [2]. Recently, the use of biomass for the production of bioadsorbents has attracted a lot of attention due to its abundance, non-toxicity and low cost [3]. In this sense, chitosan-based adsorbents have shown a relatively high removal yield and kinetics for a lot of metals due to their high nitrogen content and porosity [4]. In addition, it has been found that a modification with thiourea and magnetite nanoparticles gives these bioadsorbents a greater adsorption capacity, selectivity towards several heavy metals and high efficiency in recovery processes, this at a laboratory scale [4, 5].

The environmental evaluation is an important tool in the design and analysis of processes because its development allows to determine the degree of pollution generated in a chemical process, since it identifies the potentials toxicological and atmospheric environmental impacts [6]. Waste Reduction Algorithm (WAR) is one of the most used tool for environmental assessment, which is useful because it allows quantifying the generation of potential environmental impacts based on 8 impact categories (Bicer et al. al., 2016). In this study, the simulation of a large-scale production of chitosan micro-beads modified with thiourea and magnetite was performed using computer aided process engineering. Then, from the extended mass and energy balance obtained from simulation, the environmental assessment of the process was performed using WAR GUI software which is based on the WAR algorithm [6]. First, total impacts were calculated for different cases; then, toxicological and atmospheric impacts and, finally, the effect of three energy sources (coal, oil and gas). All these in order to find the viability of the large-scale process regarding to environmental perspective.

2. Methods

2.1. Process description

As a first stage of the process, the synthesis of the magnetite nanoparticles is carried out, and in a second stage, the production of the microbeads is developed by the co-precipitation method under alkaline conditions. Figure 1 represents the production process of the modified microbeads.

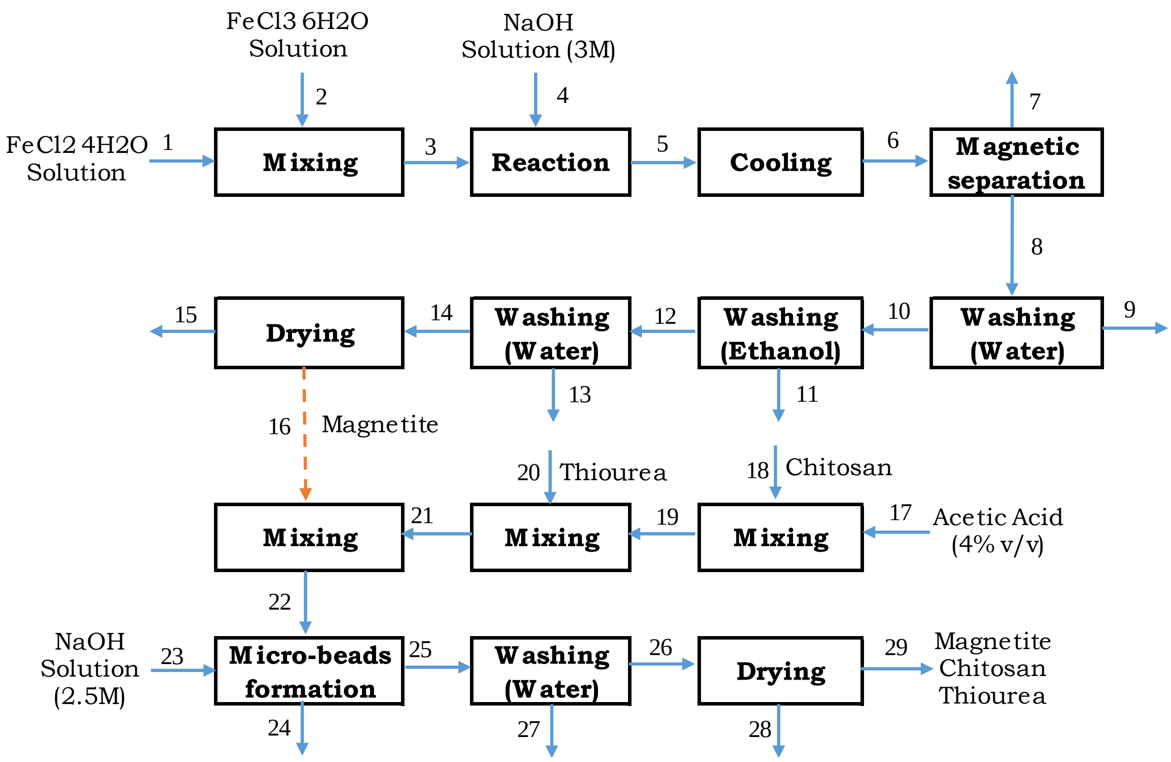

Figure 1. Block diagram of production of chitosan micro-beads modified with thiourea and magnetite.

2.1.1. Production of magnetite nanoparticles. Initially, the solutions of iron trichloride hexahydrate and iron dichloride tetrahydrate are mixed. The output stream (stream 3) is sent to the reaction stage where sodium hydroxide is added (stream4). The current leaving the reactor is cooled and then it is sent to a magnetic separator in order to remove impurities from the magnetite nanoparticles current. Finally, the nanoparticles (stream 8) are sent to a washing train with water, ethanol and water in order to stabilize the pH of the medium, and are sent to a dryer (stream 15).

2.1.2. Preparation and modification of chitosan microbeads with thiourea and magnetite nanoparticles. Initially, the chitosan (flow 18) is mixed with a solution of acetic acid (flow 17) and subsequently with thiourea (flow 20). In a next mixing step, the magnetic nanoparticles are added (stream 16) and the resulting stream (stream 21) is injected into a sodium hydroxide solution which is constantly stirred until the microbeads are formed. Finally, the residual sodium hydroxide is removed (stream 24) and the microbeads formed are washed with water and dried (stream 29).

2.2. Environmental assessment using WAR algorithm

For the environmental evaluation of the large-scale production of chitosan micro-beads modified with thiourea and magnetite, the waste algorithm reduction (WAR) methodology was selected. The WAR GUI Software was chosen due to the open availability of the software and its ability to quantify the rate of potential environmental impacts (PEI) generation (or consumption) [9], for processes considering the flow of an environmental impact across the boundaries of the system as a consequence of the mass and energy that crosses these limits [8]. This index is considered from two points of view: PEI output rate and PEI generated. The first measures the PEI impact emitted by the process to its surroundings and it is useful to solve questions about the external efficiency of the process; regarding to the second, it measures the generation of PEI within the limits of the process and it is related to the internal environmental efficiency of the process. Lower values for these indices implies that the process has a better environmental performance. The WAR algorithm considers eight impact categories, which are classified into two major groups: local toxicological impacts on humans (HTPI, HTPE) and ecological (ATP, TTP), and atmospheric which divides into global (GWP, ODP) and regional (AP, PCOP) impacts [10].

In this work, four different cases were studied: a base case without taking into account the contribution of energy resources and products flows (Case 1), and 3 cases where was considered the product stream (Case 2), the energy process (Case 3), and the amount of energy-product stream (Case 4). First, total impacts were calculated for the four cases; then, toxicological and atmospheric impacts and, finally, the effect of three energy sources (coal, oil and gas). All these in order to obtain an accurate diagnosis of the environmental viability of the large-scale process.

3. Results and Discussion

3.1. Total Potential Environmental Impacts of the process: Generated and output

From Figure 2, the total generation rate of PEI in four cases studied were negative ($-4.98x10^2$, $-1.44x10^2$, $-4,8x10^2$, $-1.26x10^2$ PEI/h for cases 1, 2, 3 and 4 respectively) which indicates that the process is environmentally friendly since the process itself does not generate environmental impacts. Regarding the total output rate of PEI, it is show that the base case and the case including energy are pretty similar (1.54x103 and 1.56x103 PEI/h) which suggest that the energy inclusion does not generate significant impacts. Otherwise, including products in the analysis entails an identical increase of impacts with respect to analysis without taking account products; this is, totals generation and output rate of PEI for cases 2 (including products) and 4 (including energy and products) are higher than cases 1 (base case) and 3 (including energy).

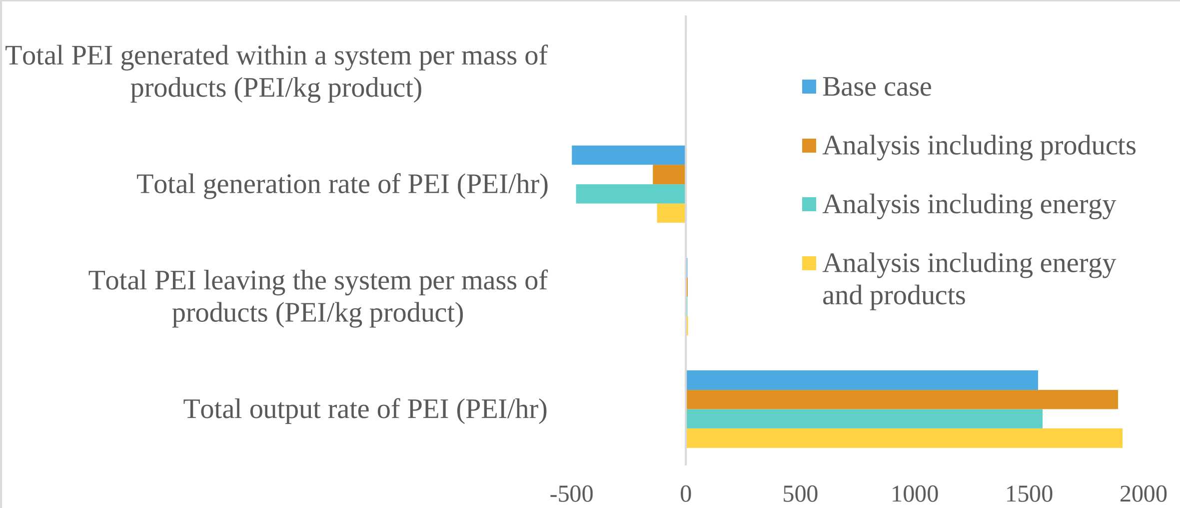

Figure 2. Total PEI generated and output of the large-scale production of chitosan micro-beads modified with thiourea and magnetite.

3.2. *Local toxicological impacts of the process*

Figure 3 shows the local output and generated toxicological impacts of the process, which include human toxicity potential by ingestion (HTPI), Human toxicity potential by inhalation or dermal exposure (HTPE), aquatic Toxicity Potential (ATP) and Terrestrial toxicity potential (TTP) impact categories. It can be evidenced that the ecological output impacts are more significant compared to the impacts directed on humans for all cases studied. Figure 3 shows that for ATP and HTPE (17.6 and 8.45 PEI/h for case 1) the total output rate of PEI were significantly lower than TTP and HTPI (in both cases equal to 285 PEI/h for case 1) categories. As regard the PEI generated, all values were negatives suggesting that the process have in the product streams, less toxic chemicals with tolerance values limits (TVL) lower than those fed to the system. Furthermore, it was observed that energy inclusion in environmental analysis had little or no effect on results obtained, having identical or very similar values for all toxicological impact categories for cases 1 and 3, and for the cases 2 and 4. It was also found that products inclusion significantly increased generated and output PEI for the process, except for HTPE which has an almost negligible increase.

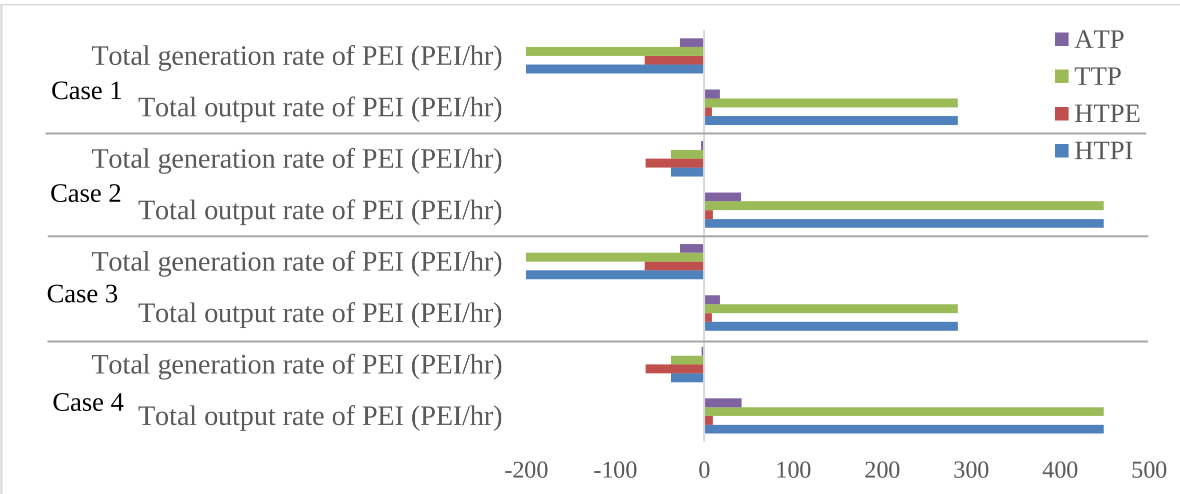

Figure 3. Local output and generated toxicological impacts of the large-scale production of chitosan micro-beads modified with thiourea and magnetite.

3.3. Atmospheric impacts of the process

Figure 4 shows output and generated atmospheric impacts of the process, which include Global Warming Potential (GWP), Ozone depletion potential (ODP), Photochemical Oxidation Potential (PCOP) and Acidification potential (AP) impact categories. For this particular process, it is observed that all the values for AP, ODP and GWP, for cases 1 and 2 are equal to zero and for cases 3 and 4 are considerably low; which leads to the conclusion that this process is environmentally neutral under these categories, so the greatest contribution to PEI out for atmospheric categories comes from the use of fuels in the process as energy sources, as in cases 3 and 4.

PEI output for GWP (1.55 PEI / h) and AP (16.1 PEI / h) impact categories, in cases 3 and 4, indicates that this process emits chemical substances that persist longer in the environment due to their low oxidation and also can contribute to the generation of acid rain.

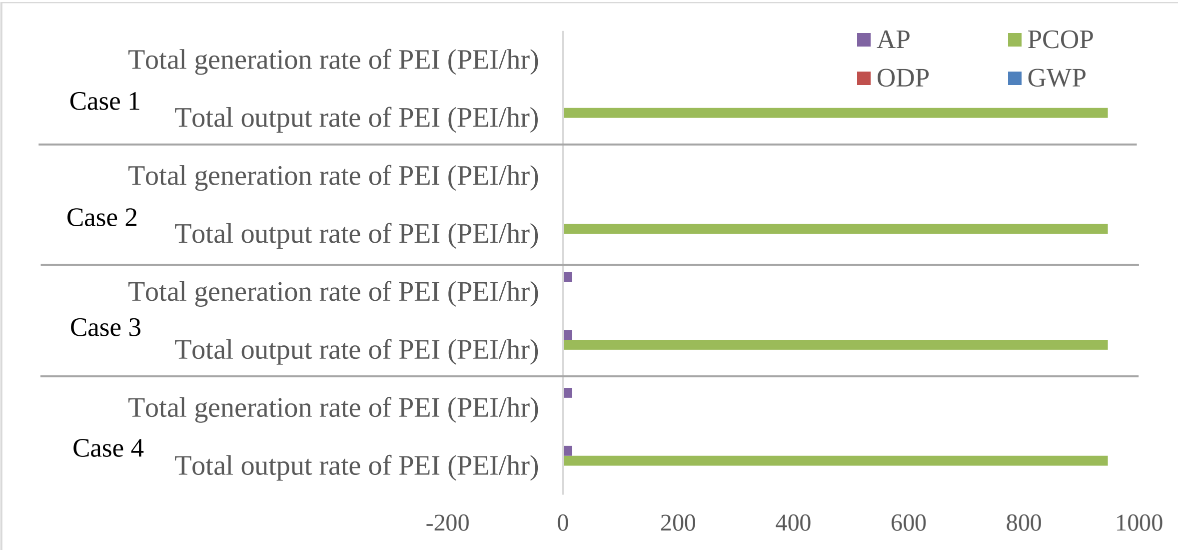

Figure 4. Output and generated atmospheric impacts of the large-scale production of chitosan micro-beads modified with thiourea and magnetite.

3.4. Effect of energy source

Figure 5 shows the effect of energy source on the eight impact categories total output rate of PEI, for three types of fuel (gas, oil and coal), including energy and excluding product stream. It was found that most of the impact categories show very little or no variation due to the fuel used, except for AP impacts where coal usage increases the impact (96.9 PEI/h). Compared to the global output rate of PEI for the process, the PEI from energy source do not represent many concerns because its contribution is lower considering other effects previously described, so this process has a good energetic performance from an environmental point of view. It can be observed that gas had a better performance compared to the others energy sources because it has less or equal impact on all categories taken into account.

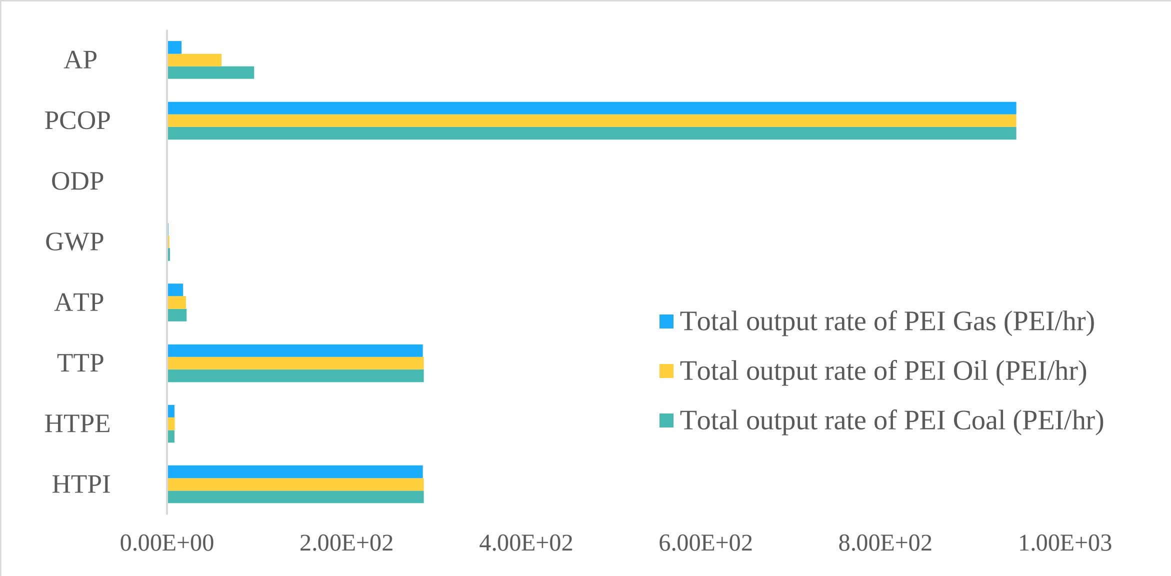

Figure 5. Effect of energy source on the output rate from energy usage for the large-scale production of chitosan micro-beads modified with thiourea and magnetite.

4. Conclusions

Waste Reduction Algorithm (WAR) was implemented for environmental assessment of a large-scale production of chitosan micro-beads modified with thiourea and magnetite. From results obtained, it can be said that the process is beneficial in environmental terms because it transforms the feed streams of high PEI into final products of lower PEI, which is manifested by the negative values of total generation rate of PEI in all the cases. It was also found that energy does not generate significant impacts on total PEI.

Regarding to toxicological impacts, it can be evidenced that the ecological output impacts are more significant compared to the impacts directed on humans for the four cases studied. For these impact categories, all PEI generated values were negatives implying that product streams are less toxic chemicals than those fed to the process. With respect to atmospheric impacts it can be affirmed that the process is environmentally neutral under ODP and GWP categories, so the highest contribution to PEI output for atmospheric categories occurs by the usage of fuels in the process as energy sources. Results shows that PCOP is the evaluated category which emits the most output PEI, contributing in all cases between 49.4 and 61.43% of the total output PEI, which is attributed to the presence of ethanol in the washing stages. Therefore, a way to reduce these environmental impacts involves replacing the ethanol by another solvent which has less environmental impact. Furthermore, this process emits chemical that persist longer in the environment due to their low oxidation and can also contribute to the generation of acid rain.

Acknowledgments

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