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Analyzing Environmental Impacts of Hypercrosslinked Polymers Produced from Continuous Flow Synthesis for Water Treatment

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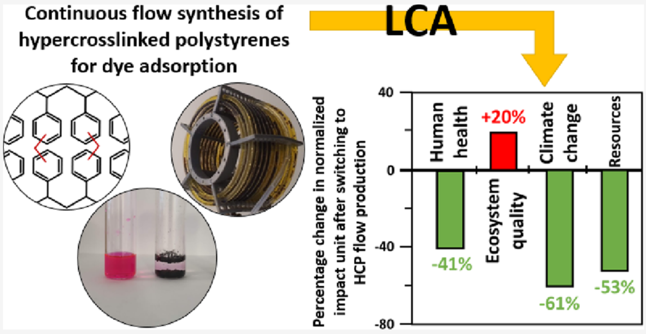

ABSTRACT: Polymer production in the 21stcentury will require alternative approaches that do not impact the environment negatively. We recently reported that the synthesis of hypercrosslinked polymers (HCPs) *via* continuous flow synthesis required less than 99% of the time required in conventional batch reactions. However, the impact of deploying flow synthesis of HCPs and their application on the environment remain unknown. Here, we assessed the environmental impacts of HCP synthesis *via* batch and flow reactions and their application in water treatment through life-cycle assessment (LCA). These impacts were represented as normalized scores in four end point impact categories: Human health, Ecosystem quality, Climate change, and Resources. Yielding the same amount of HCPs, flow synthesis demonstrated lower end point impacts in all categories. This was due to consuming only 5% of the electricity required for batch reactions. As the specific surface areas of flow-produced HCPs were lower than those of batch-produced HCPs, 36% more flow-produced HCPs were required to remove Rhodamine B (RB) and Uniblue A (UA) dyes from water. Despite this limitation, using flow-produced HCPs for water treatment still scored lower overall negative environmental impacts when compared to batch-produced HCPs. Outcomes from this work showed that flow synthesis could enhance the sustainability of scale-up HCP production.

1. INTRODUCTION

Continuous flow synthesis has been widely employed for process intensification in the production of fine chemicals[1] and pharmaceuticals[2] in the last two decades.[3] Compared with batch reactors, flow reactors possess a higher surface area to volume ratio[4] that improves heat and mass transfers, which enhances reaction kinetics.[5,6] Other advantages associated with flow synthesis include ease of scale-up[7] and safer reactions that involve hazardous chemicals or harsh operating conditions.[8]

Continuous flow reactions have also been exploited for synthesizing microporous materials, such as metal−organic frameworks (MOFs),[7] covalent organic frameworks (COFs),[9] and polymers of intrinsic microporosity (PIMs).[10] We recently demonstrated that hypercrosslinked polymers (HCPs) could be synthesized[11] and optimized[12] *via* continuous flow reactions. HCPs are polymeric microporous adsorbents that possess extensive rigid yet flexible crosslinked structures that expand while adsorbing organic solvents.[13] The advantages of synthesizing HCPs in flow reactors include (1) reducing synthesis duration by more than 99% and improving space−time yield (STY) by 32-fold, (2) improving reaction kinetics to yield HCPs with higher microporosity when compared to those synthesized in batch reactors, and (3) improving CO_2/N_2 selectivity of HCPs by 9.5-fold. As such, continuous flow syntheses could potentially scale up the production of highly selective HCPs. Despite demonstrating the feasibility of continuous flow synthesis of HCPs, the sustainability of this process has not been evaluated. For example, other than improving productivity rates, will reducing synthesis duration benefit the environment? Will the lower specific surface areas of flow-produced HCPs create negative impacts on the environment when deployed in applications?

The most logical and scientific way to answer these questions and evaluate the sustainability of HCP flow syntheses towards the environment is to quantify the term "sustainability". For example, life-cycle assessment (LCA) is widely used to assess the potential impact of processes based on quantitative modeling.[14,15] Following the standard of the ISO 14040 and ISO 14044 frameworks,[16] there are four stages in an LCA: Goal definition, Scope definition, Inventory analysis, and Impact assessment. Briefly, the study will clearly describe why an LCA is required. This would suggest what the functional unit of the LCA should be. The functional unit is the key quantified description to which all calculations will be

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referenced. The practitioner will then set up boundaries of the study consisting of foreground processes (visible processes where first-hand data could be retrieved by the practitioner) and elementary flows (resources, emissions, materials, waste, electricity, heating, etc.) showing as input and output flows. These flows will be categorized and summed up in an inventory table. Data from background processes (*i.e.*, upstream processes), usually retrieved from commercial databases, are also taken into account at this stage. Then, the analysis will be performed based on selected impact assessment methods that allow the practitioner to understand the environmental impacts and answer questions underpinning the intention that was defined at the start of the LCA design.

LCA has been utilized for evaluating various products, processes, or services. For instance, an LCA was performed for laboratory-scale graphene production with an intention to identify a production method with the lowest environmental impact from three different options that were based on small-scale process assessments.[17] Meanwhile, an LCA was also performed to identify the most efficient and sustainable route for synthesizing porous polymers from Kraft black liquor.[18] The motivation for performing this LCA was to evaluate if recycling and reusing solvents used in this process could lower its environmental impact when compared to the traditional process that currently uses single-use solvents. The LCA outcome showed that there were several trade-offs between these two scenarios, and neither scenario was the best in all impact categories. This showed that unless an LCA was performed, there is no way to verify if the alternative approach was indeed better than the original route. Vladisavljevic *et al.*[19] performed an LCA to compare the environmental impacts of producing seven different amide-based polymer sorbents using a functional unit of 1 kg of captured CO_2. In this study, the authors put emphasis on the differences in adsorption capacity and selectivity between the proposed polymers and conventional molecularly imprinted polymers. Taking into account the adsorption performances of these sorbents, the LCA revealed that low quantities of HCPs were required to capture the same amount of CO_2 when compared to molecularly imprinted polymers, resulting in lower environmental impacts. By considering product utilization, this assessment evaluated more than half of the life cycle of the products.

Besides gas separation, HCPs have also been deployed as adsorbents in water treatment,[20,21] removing ecotoxic dyes from the wastewater effluent from several industries.[22−24] Examples of such dyes include Rhodamine B (RB), a magenta-colored, carcinogenic, and neurotoxic dye commonly found in textiles, paints, and fireworks,[25,26] and Uniblue A (UA), a blue-colored dye commonly used in the textile industry.[27] We recently also showed that waste expanded polystyrene (trade name Styrofoam) can be recycled into HCPs for removing these dyes from water, with adsorption capacities of RB and UA reaching values of 552 and 1098 mg g^{-1}, respectively.[23] However, the synthesis of these highly microporous HCPs from Styrofoam waste (Brunauer−Emmett−Teller surface area reaching 1250 m^2 g^{-1}) required 5 times more the reagents deployed in HCP synthesis from monomers. This may offset the sustainability of upcycling one of the last-recycled plastic waste into advanced materials for water treatment *via* adsorption. Moreover, the actual impact and benefits of this approach remain unknown.

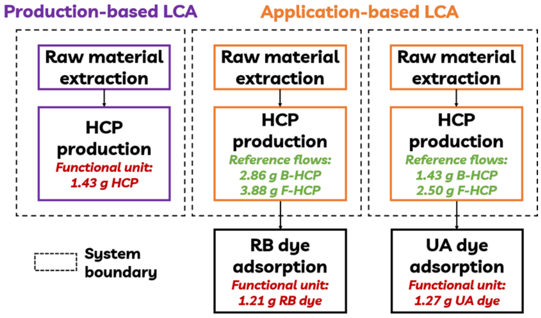
In this work, we evaluated the environmental impacts of upcycling Styrofoam into HCPs *via* batch and flow reactions and their application in dye removal. This was achieved with two LCA main cases. The first LCA was based on the differences in synthesis methods: flow vs batch reactions. The goal of this LCA was to determine and compare the environmental impacts of producing approximately 1.5 g of HCPs *via* batch and flow reactions. The second LCA was application-based, focusing on evaluating the environmental impacts of deploying HCPs from batch or flow syntheses for dye removal *via* physisorption. This was based on the minimal amount of HCPs from each synthesis approach for removing about 1.2 g mL^{-1} of dyes. The scope of both LCAs was cradle-to-gate where the production of raw materials for HCP syntheses was also evaluated.[19,28] The process was then modeled in the inventory analysis stage. We used the IMPACT 2002+ methodology for impact assessment, categorizing environmental impacts into four end-point-level impact categories: Human health, Ecosystem quality, Climate change, and Resources. Throughout these four categories of assessments, we determined how environmental impacts changed as a function of synthesis approach deployed in producing HCPs for water treatment. Outcomes from these studies demonstrated that continuous flow reactions improved the environmental impacts of HCP synthesis. The high productivity rates and improved environmental impacts of continuous flow synthesis suggested that this approach could be beneficial for HCP production at a mass manufacturing scale.

2. EXPERIMENTAL SECTION

2.1. Goal Definition. The aim of this work was to evaluate if continuous flow reactions improved the environmental impacts of HCP synthesis. Two LCAs were performed in this work. The first LCA was conducted to compare the difference in environmental impacts between conventional batch reactions and the new approach of flow synthesis based on the same quantity of HCPs produced from each method. The goal of this process based LCA was to identify the cause, *i.e.*, hotspots, of the environmental impacts of each synthesis approach and establish the differences in these impacts. The second LCA was performed to evaluate the difference in environmental impacts from the perspective of deploying the same amount of HCPs, produced from two different approaches, in dye adsorption for applications in water treatment. The goal of the second LCA was to elucidate if flow synthesis minimized the negative environmental impacts of HCP application despite requiring more materials due to the lower specific surface areas of flow-produced HCPs.

2.2. Scope Definition. The two LCA cases in this study were differentiated by their functional units (Scheme 1). The

Scheme 1. Functional Units and Reference Flows of Production-Based LCA and Application-Based LCA



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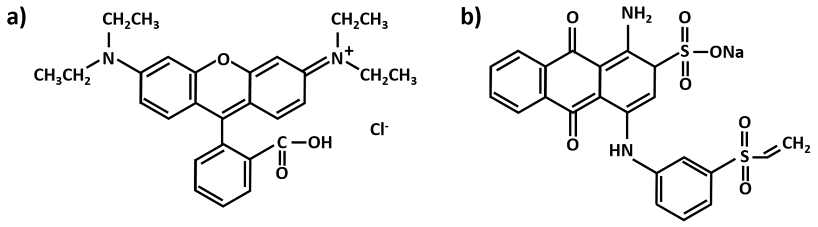


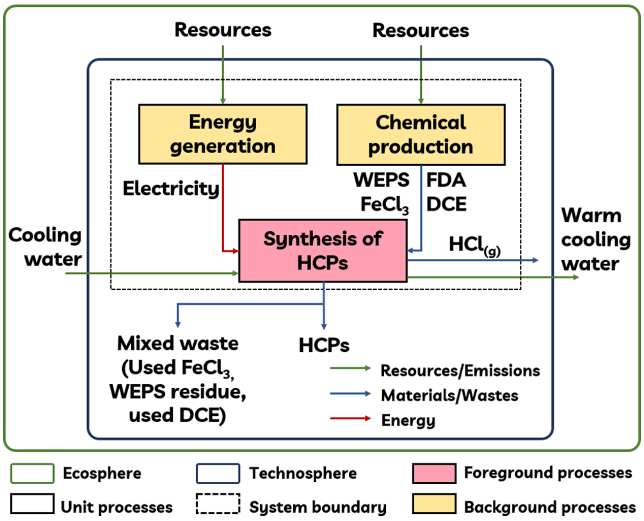
Figure 1. Dye molecules: (a) Rhodamine B (RB) and (b) Uniblue A (UA).

reason for two separated functional units was to answer whether, in case flow synthesis shows less environmental impacts than batch synthesis for the same amount of synthesized HCP, flow synthesis would still create less impacts when the amount of synthesized HCP is different between batch and flow reactions (which causes the difference in performance ability). The type of HCP selected for this study was derived from polystyrene that was externally crosslinked using formaldehyde dimethyl acetal (FDA). Batch-produced HCP and flow-produced HCP were denoted as B-HCP and F-HCP.

The functional unit of the process-based LCA was set to 1.43 g of HCP synthesized from batch and flow reactions. In the second LCA, two subcases were conducted representing two scenarios in which HCPs were utilized for removing RB and UA from water *via* adsorption (Figure 1). The functional units of these two LCA subcases were assigned as removing 1.21 g of RB and 1.27 of UA from water using B-HCP and F-HCP. On the basis of isothermal adsorption analyses (see the Supporting Information), the required masses of B-HCP and F-HCP for adsorbing 1.21 g of RB dyes were 2.86 and 3.88 g, respectively. Similarly, for adsorbing 1.27 g of UA dye, 1.43 g of B-HCP and 2.05 g of F-HCP were required.

The system boundaries of our LCAs (inside the dotted boxes in Schemes 1 and 2) included only raw material extraction and HCP synthesis stages. The inlet and outlet flows of the dye adsorption stage were omitted from environmental impact assessments here. This was due to the objective of the study to put emphasis on the comparison of environmental impacts created from the synthesis of HCPs between batch and flow reaction. Waste disposal, adsorbent regeneration, and solvent recycling stages were negligible. We also excluded the impacts of material transport and infrastructure processes from these studies because of the lack of precise information associated with these factors. Although the production of HCPs was achieved through lab-scale experiments at the School of Engineering, The University of Edinburgh, some inputs such as raw chemicals and electricity were produced within the E.U. Hence, the geological scope in this work was European.

Scheme 2. Details of Inlet and Outlet Flows across the System Boundary of All LCAs in This Study



2.3. Inventory Analysis.

2.3.1. Foreground Processes. Here, we regarded the synthesis stage as the foreground process. This inferred that primary data such as chemical and electricity consumption were collected directly from the laboratory. The total electricity usage was measured using an RS PRO digital plug-in energy meter (RS 178-5373).

The procedure for batch synthesis was as follows: Waste-expanded polystyrene (WEPS) was dissolved in 1,2-dichloroethane (DCE) in a 250 mL three-neck round flask. Iron(III) chloride ($FeCl_3$) and formaldehyde dimethyl acetal (FDA) were added into the mixture. A water-cooled condenser column was used to create a reflux system so that evaporated DCE could be condensed and reused in the reaction. Then, the mixture was heated at 80 °C while stirring with magnetic stirrer. We observed that gelation of this mixture occurred after 20−30 min of the reaction. This was common in batch HCP synthesis as the newly formed microporous HCPs adsorbed solvent molecules. At this point, we added 10−50 mL of DCE into the reactor, breaking up the gel so that stirring could carry on. After 24 h, the batch reaction was stopped by allowing the mixture to cool down to room temperature (25 °C). A sludge product was obtained, filtered, and washed with chloroform, excess methanol, and excess acetone consecutively. Then, the washed product was soaked in methanol overnight. Finally, the product was dried in an oven at 60 °C overnight.

The procedure for flow synthesis was as follows: Substrate feed was prepared by dissolving WEPs in DCE. This solution was loaded into a syringe prior to feeding into a polytetrafluoroethylene tube reactor (30 mL reactor volume, 1.58 mm inner diameter tube)[12] that was submerged in a 70 °C oil bath *via* a syringe pump (Cole-Parmer SP210iwz). A catalyst feed solution was prepared by mixing $FeCl_3$ and FDA in a separate solution of DCE. The catalyst feed was fed into the flow reactor *via* a peristaltic pump (SEKO Kronos 50). Both substrate and catalyst solutions were fed into the reactor, *via* a Y-junction where these solutions were mixed, with a total flow rate of 1.94 mL min^{-1}. Solid particles were extruded from the end of the reactor as a brownish sludge in the glass container at the end of the tube. The sludge product from flow synthesis was filtered, washed, and dried in the same method as the sludge product from batch synthesis.

2.3.2. Background Processes. Data for raw material extraction stage were obtained from ecoinvent 3, a Swiss-based commercial database that provided the models of

Table 1. Details of Data Collection Stage

products/services	processes	specificities	sources	accesses
batch-produced HCPs	Friedel−Crafts alkylation	very high	LCA practitioner	first-hand gathering
flow-produced HCPs	Friedel−Crafts alkylation	very high	LCA practitioner	first-hand gathering
expanded polystyrene (WEPS)	suspension polymerization of ethylene and benzene	medium	ecoinvent 3	database search
ethylene dichloride (DCE)	direct chlorination of ethylene	medium	ecoinvent 3	database search
iron(III) chloride ($FeCl_3$), without water, in 40% solution state	oxidization of iron scape and $FeCl_2$ with chlorine gas	medium	ecoinvent 3	database search
electricity, medium voltage	natural gas (conventional power plant), hard coal, nuclear (pressure water reactor), etc.	medium	ecoinvent 3	database search
formaldehyde dimethyl acetal (FDA)	condensation from methanol and formaldehyde	low	previous LCI literature	online journal search[29]

approximately 12,500 processes, ranging from solvent production to electricity generation in various regions to transportation. These models contained mathematical inputs (resources) and outputs (emission) produced from the process. However, a model of the FDA production process was not available in this database. Hence, this process was created manually by importing inventory data related to this process from another relevant LCA study.[29]

2.3.3. Dye Adsorption Test. To conduct the second LCA, isothermal dye adsorption experiments were performed to determine the required quantities of B-HCP and F-HCP for RB and UA adsorption. The procedure was described as follows: Dye solutions were prepared at different concentrations within the range of 20−1000 mg L^{-1} by dissolving dye powders in deionized water. HCP samples (5 g) were added into 5 mL of dye solutions of each concentration. These mixtures were left undisturbed until the equilibrium state was reached. The remaining dye concentration in these solutions was determined using a UV−vis spectrometer. The empirical adsorption isotherm was plotted between the equilibrium adsorption capacity, Q_e [mg g^{-1}], and the equilibrium dye concentration, C_e [mg L^{-1}]. C_e referred to the concentration of the remaining dye solutions, whereas Q_e was determined with the following equation:

$$Q_e = (C_0 - C_e)\frac{V}{m}$$

It should be noted that C_e was not an independent variable in the adsorption test; thus, the range of C_e would be different for each adsorption test (different HCP types in different dyes).

Langmuir and Freundlich adsorption isotherms were fitted to determine if dye adsorption in B-HCP and F-HCP was monolayer or multilayer. The equations were as follows:

$$\text{Langmuir adsorption: } Q_e = \frac{Q_m K_L C_e}{1 + K_L C_e}$$

$$\text{Freundlich adsorption: } Q_e = K_F C_e^{1/n}$$

C_0 [mg L^{-1}] was the initial concentration of the dye solution, V [mL] was the volume of the dye solution, m [mg] was the mass of the HCP sample, K_L [L mg^{-1}] was the Langmuir constant associated with the binding energy that indicated how strong the interaction between dye molecules and the HCP surface is, Q_m [mg g^{-1}] referred to the maximum adsorption capacity, K_F [$L^{1/n}$ $mg^{1-1/n}$ g^{-1}] was the Freundlich constant related to adsorption capacity, and $\frac{1}{n}$ was the Freundlich constant related to sorption intensity. As Langmuir and Freundlich adsorption models are empirical formulas, the values of K_L, Q_m, K_F, and $\frac{1}{n}$ parameters were then determined through the regression method.

2.4. Impact Assessment. We deployed the black-box tool to calculate the environmental impacts using the IMPACT 2002+ V2.11 assessment tool.[30] This method was chosen here as it had been used in a similar LCA that focused on the production of hypercrosslinked methacrylamide.[19] This method provided 15 midpoint impact categories: Aquatic acidification, Aquatic eutrophication, Ozone layer depletion, Mineral extraction, Ionizing radiation, Aquatic ecotoxicity, Land occupation, Respiratory organics, Terrestrial ecotoxicity, Terrestrial acidification/nutrification, Noncarcinogens, Carcinogens, Respiratory inorganics, Global warming, and Nonrenewable energy. These midpoint categories can be grouped into four impact categories at the end point level: Human health, Ecosystem quality, Climate change, and Resources. The connection between impact categories at the midpoint and endpoint level is shown in the Supporting Information.

Quantification of environmental impacts was presented here as normalized scores. The normalization in the IMPACT 2002+ method was determined by dividing the impact score by the total impacts within the same impact category per person per year. This step was automatically compiled *via* the modeling software.

3. RESULTS AND DISCUSSION

3.1. Process Model Description. The reliability of the data was measured from the start of the data collection stage. Hence, it was necessary to present the quality of the data, *i.e.*, the specificity, the sources, and the accessibility. Table 1 shows the description of the processes involved in this study and details of the data collection step. The excluded process was the transportation of reagents and solvents from the manufacturers to the laboratory. The physical infrastructure of the laboratory, *e.g.*, electricity for lighting and ventilation, was also excluded from the modeling.

Data from Table 1 were combined to create a model that correlated to the goal and scope definitions of the LCA. The model for this LCA was conducted through SimiPro 8.0.3.14, an LCA modeling software that provides some life-cycle inventory databases and life-cycle inventory analysis methods.

3.2. Constraints and Assumptions. The constraints and assumptions from the life-cycle inventory analysis stage were outlined as follows: (1) Electricity and other utility consumptions during preheating and cleaning of equipment were exempted from the study. (2) Hydrochloric gas byproduct was excluded because of the insignificant amount. The collection method and the quantity of hydrochloric gas produced from each synthetic approach are reported in the Supporting Information. (3) WEPS residual after the filtration stage was negligible. (4) Electricity consumption in the drying stage was excluded. (5) Temperature change between inlet and outlet cooling water was negligible.

3.3. Production-Based LCA: the Comparison of Environmental Impact from the Production of 1.43 g of HCP *via* Batch and Flow Syntheses.

3.3.1. Life-Cycle Inventory. The inventory data for the first LCA are shown in Table 2. The aim of this LCA was to identify the differences in environmental impacts of HCP synthesis *via* batch and flow reactions. The functional unit in this case was chosen as 1.43 g of HCPs. Synthesizing this amount of HCPs in batch and flow reactions required 24 h and 1 h and 40 min, respectively.

Table 2. Inventory Items for the First LCA Study in Which the Functional Unit Was the Synthesis of 1.43 g of HCPs

subject	unit	batch	flow
products			
HCPs	g	1.43	1.43
chemicals			
WEPS	g	0.914	1.25
$FeCl_3$	g	4.57	6.27
FDA	g	4.57	6.27
DCE	g	150	206
other utilities			
electricity	kWh	2.30	0.203
cooling water	m^3	0.864	N/A

3.3.2. Impact Assessment. The midpoint level impact representing the intermediate position on the impact pathway was used for hotspot investigation. The top three midpoint categories with the highest impact scores from batch and flow syntheses of 1.43 g of HCPs (Figure 2) were Nonrenewable energy, Global warming, and Respiratory inorganics. Each total impact unit was split into several color blocks to indicate the impact contribution of all elementary flows, *i.e.*, chemicals and utilities in the system.

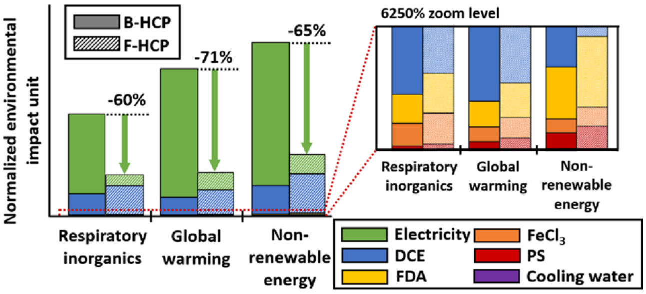


Figure 2. Top three environmental midpoint category impacts of the first LCA study in which the functional unit is the production of 1.43 g of HCP. Opaque bar charts refer to impacts from the synthesis of B-HCP. Stripe pattern bar charts refer to impacts from the synthesis of F-HCP.

We observed a huge score gap in the three midpoint impacts of Nonrenewable energy, Global warming, and Respiratory inorganics between batch and flow syntheses. Electricity was the major contributor of these gaps as the impact scores of those three highest midpoint impacts created from electricity consumption in flow production were lower by 86.7% for all three mentioned impacts. This was reasonable as synthesis duration of batch reactions was 95% more than flow synthesis, hence consuming more electricity for heating. As electricity is mostly generated from primary nonrenewable energy, *i.e.*, natural gas (the proportion of resources for electricity generation is shown in the Supporting Information), electricity consumption here could be quantified by the equivalent units of resource consumption and emissions, *i.e.*, emitted CO_2 and $PM_{2.5}$.

DCE use in flow synthesis of HCPs generated higher impacts in several categories when compared to batch synthesis. The impact scores of Nonrenewable energy created by DCE in flow synthesis were 37.2% higher than those in batch reactions. This was because the HCP yield from flow synthesis was 42.1% lower than those of batch reactions. As such, according to Table 2, more reagents were used to synthesize 1.43 g of HCPs in flow reactions; hence, more DCE was consumed. Although the impact contribution from reactants was also higher in flow synthesis, they were insignificant compared to the impacts created from solvents after the normalization of impact scores.

The environmental impacts at the end point level in Figure 3 indicated that flow synthesis created a lower impact in all end point categories when compared to batch reactions. The largest decrease was the impact toward Climate change that was reduced by 71%, followed by a 65% decrease in Resources and a 56% reduction in Human health. The large gaps in these three end point impacts were related to the high normalized midpoint category impact unit of Nonrenewable energy, Global warming, and Respiratory inorganics, respectively, as mentioned earlier. The smallest reduction in environmental impact was in Ecosystem quality; flow reactions only reduced this factor by 11%. This proved that flow synthesis of HCPs did not negatively affect the environment as much as traditional batch synthesis of the same amount of HCPs, offering a more sustainable approach to synthesize HCPs. However, this does not mean that application of flow-synthesized HCPs would reduce the environmental impacts.

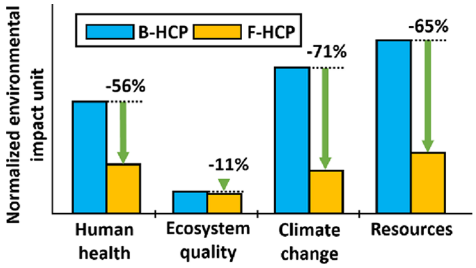


Figure 3. Normalized end-point-level impact assessments of the first LCA study in which the functional unit is the production of 1.43 g of HCP.

3.4. Application-Based LCA: Environmental Impact from the HCP Synthesis for Dye Adsorption.

3.4.1. Dye Adsorption Performance. The second LCA study aimed to determine and compare the environmental impacts created from batch and flow syntheses of the required amount of HCPs for removing the same amount of RB and UA from water *via* adsorption. Isothermal dye adsorption experiments were conducted to determine the maximum adsorption capacity of B-HCP and F-HCP for each dye type. These values were then used to calculate the required amount to adsorb an amount of dye (the functional unit of the second LCA study). Curve fitting of experimental adsorption isotherm data of B-HCP and F-HCP using Langmuir and Freundlich models shown in Figure 4 was used here to evaluate the adsorption behavior of these HCP samples. Clearly, the equilibrium dye concentration of the UA solution was lower than that of the RB solution, indicating that HCPs adsorbed more UA molecules than RB molecules. With higher R^2 values (Table 3), the Langmuir model was able to describe the dye adsorption behavior of both B-HCP and F-HCP. This indicated that the adsorption behavior of all HCPs was homogeneous, in which the adsorption capacity was limited when all sorption sites are nonvacant (monolayer adsorption).[23] The adsorption behavior of B-HCP and F-HCP in RB and UA solutions, *i.e.*, maximum adsorption capacity (Q_m), was used here in this work to calculate the required amount of HCPs for dye adsorption.

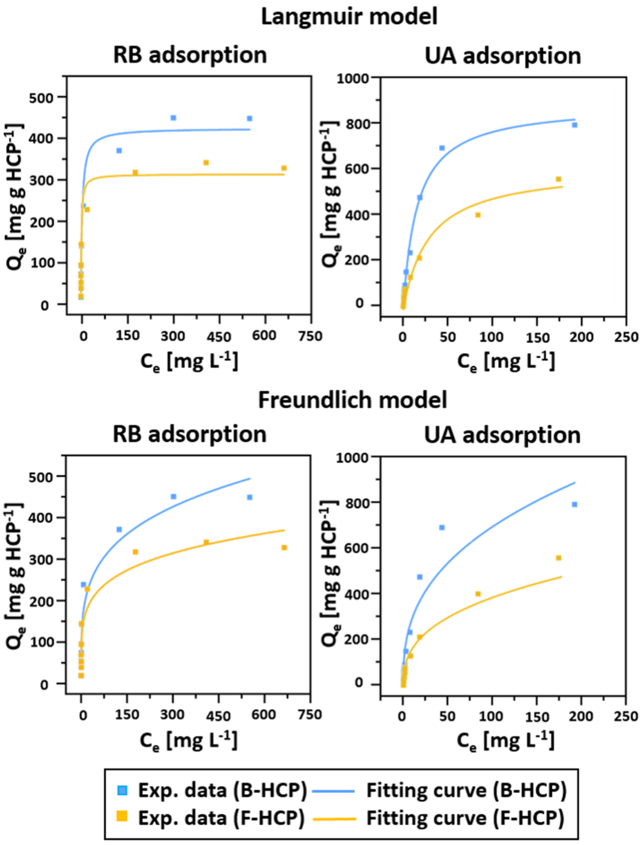


Figure 4. Adsorption isotherms.

Table 3. Adsorption Isotherm Parameters

dyes	synthetic methods	Langmuir model			Freundlich model		
		K_L	Q_m	R^2	K_F	$1/n$	R^2
RB	batch	0.245	424	0.967	106	0.243	0.952
	flow	0.613	313	0.958	98.1	0.204	0.920
UA	batch	0.062	887	0.992	123	0.376	0.903
	flow	0.035	619	0.978	77.7	0.353	0.960

3.4.2. Life-Cycle Inventory. The inventory data for the second LCA that assessed the environmental impacts of using the minimum amount of B-HCP and F-HCP to adsorb RB and UA dyes are shown in Table 4. The functional units in the two subcases were removing 1.21 g of RB and 1.27 g of UA from 12 L of water *via* adsorption with B-HCP and F-HCP. The required weights of B-HCP and F-HCP then became reference flow inputs of the second LCA model. According to the selected functional unit, the required amounts of B-HCP and F-HCP were 2.86 and 3.88 g, respectively, for RB adsorption and 1.43 and 2.05 g, respectively, for UA adsorption (Scheme 1).

Table 4. Inventory Items for the Second LCA Study in Which Environmental Impacts Were Assessed on the Production of the Required Amount of B-HCP and F-HCP for 1.21 g RB and 1.27 g UA Adsorption

subject	unit	RB (1.21 g)		UA (1.27 g)	
		batch	flow	batch	flow
products					
HCPs	g	2.86	3.88	1.43	2.05
chemicals					
WEPS	g	1.83	3.39	0.914	1.80
$FeCl_3$	g	9.14	17.0	4.57	8.98
FDA	g	9.14	17.0	4.57	8.98
DCE	g	300	557	150	295
other utilities					
electricity	kWh	4.59	0.497	2.30	0.277
cooling water	m^3	1.73		0.864	

3.4.3. Impact Assessment. The life-cycle impact assessments for the two subcases of the second LCA study are presented as normalized end point category impacts in Figure 5. According to Table 4, the amounts of F-HCPs used for RB and UA adsorption were higher than those of B-HCPs by 36 and 43%, respectively. This was ascribed to their lower adsorption capacity (Table 3). Hence, the difference in impact scores between batch and flow was different from the first LCA case. The impacts of Climate change, Resources, and Human

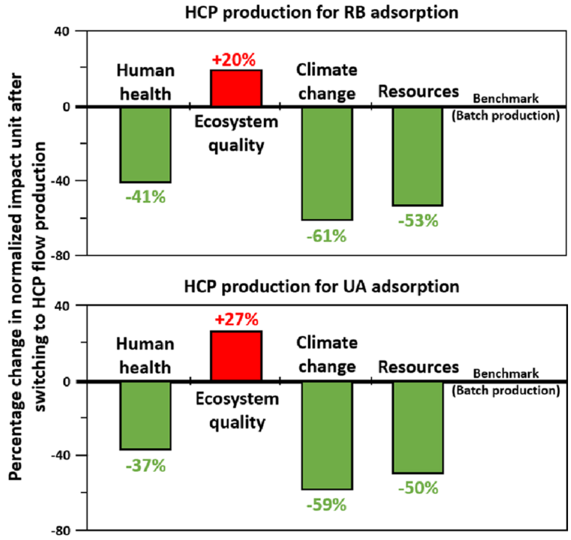


Figure 5. Percentage changes in normalized end point category impacts from HCP production after switching to the flow approach. The functional unit is based on 1.21 g of RB and 1.27 g of UA to be adsorbed.

health for flow synthesis of 3.88 g of F-HCPs were 61, 53, and 41% lower than those from batch synthesis of 2.86 g of B-HCP for adsorbing 1.21 g of RB. Similarly, the impacts toward these three impact categories for adsorbing 1.27 g of UA dye with 2.05 g of F-HCPs were 59, 50, and 37% lower than using 1.43 g of B-HCPs. This could be due to the impact associated with electricity consumption (which was the major contributor according to the first LCA result) in the production of B-HCP. This highlighted the advantage of flow synthesis as this approach could create lower environmental impacts in terms of Climate change and Resources while producing more product. Meanwhile, the impact scores of Ecosystem quality from flow-produced HCPs for RB and UA adsorption were higher than those of HCPs yielded from batch reactions by 20 and 27%, respectively. However, the score from this category was still relatively low when compared to the normalized scores of the other three end-point-level impacts.

4. CONCLUSIONS

The comparison of environmental impacts of HCP production between traditional batch and flow syntheses was revealed in this study to prove the sustainability of flow HCP synthesis. Through LCA, the impact assessment showed that on the basis of the production of 1.43 g of HCP, flow production provided lower impact scores in all four end-point-level categories, consisting of Human health, Ecosystem quality, Climate change, and Resources, by 56, 11, 71, and 65%, respectively. This was primarily due to the decrease in electricity consumption in flow production in which it required only 5% of traditional batch reaction time. The flow system also provided lower environmental impacts than the batch system when a higher amount of F-HCP was produced for dye adsorption application. When 1.21 g of RB and 1.27 g of UA needed to be adsorbed, F-HCP was required higher than B-HCP by 36 and 43%, respectively, as F-HCP had lower adsorption capacity. The impact scores of Climate change, Resources, and Human health from the production of 3.88 g of F-HCP were lower by 61, 53, and 41% than the production of 2.86 g of B-HCP for RB adsorption. The impact scores from the same three end point categories were similar in the adsorption of UA scenario, as the production of 2.05 g of F-HCP created lower scores than the production of 1.43 g of B-HCP by 59, 50, and 37%. There is a suggestion that become noticeable after the conduction of LCA to improve the level of sustainability of the flow process. Higher DCE consumption in flow production was observed in both assessments. This had a negative effect toward the Ecosystem quality category by 20 and 27% in RB and UA adsorption, respectively. The substitution of current halogenated solvent (DCE) to the environment-friendlier chemicals could help lower impacts created from the proposed flow production.

Moreover, there are several suggestions that can improve the reliability of the assessment. First, an uncertainty analysis and sensitivity study would confirm the reliability of the LCA model as the background process of FDA is missing from the ecoinvent database. Second, an environmental assessment of the pilot scale production should be conducted. This would require the validation of the pilot plant continuous flow reactor that should be redesigned and further investigated. Third, the regeneration of HCPs should be included in the study. This would lower the amount of utilized HCPs for the specific application. However, other elements involving the regeneration of such solvents or electricity might need to be considered. Fourth, the heat transfer within the system could be reused from one place to other. This would help lower the input of heat of the whole system. Yet, the pilot scale flow synthesis process is required before this step could be conducted.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.3c00829.

> The document includes (1) the pathway of the impact from IMPACT 2002+ method, (2) the description for the HCl gas collection experiment, (3) the inventory of the background processes from ecoinvent, (4) the UV−vis spectra and calibration curve of RB and UB dyes at different initial concentrations, and (5) the impact scores from three LCA cases (PDF)

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Author Contributions

The study was proposed by N.C. The conceptualized idea was discussed between N.C. and C.L. The experimental part (synthesizing HCPs and dye adsorption test) was conducted by N.C. Modeling of LCA and result analyzing were done by N.C. The paper was prepared by N.C. with supervision from C.L.

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Notes

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■ ABBREVIATIONS

HCP	hypercrosslinked polymer
LCA	life-cycle assessment
RB	Rhodamine B
UA	Uniblue A
B-HCP	batch-produced hypercrosslinked polymer
F-HCP	flow-produced hypercrosslinked polymer

WEPS	waste-expanded polystyrene
DCE	1,2-dichloroethane
$FeCl_3$	iron(III) chloride
FDA	formaldehyde dimethyl acetal

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