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## Innovative benign-by-design flow chemistry protocols

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## **Innovative benign-by-design flow chemistry protocols: from bio(nano)materials synthesis to biomass/waste valorisation**

**KEYWORDS:** Biomaterials, microfluidic fabrication, continuous flow process, wastewater treatment, catalytic application.

**ABSTRACT:** Biomaterials featuring outstanding natural properties have shown promising potential for numerous applications, especially in wastewater treatment and catalysis. This contribution aims to briefly introduce the concepts of microfluidic fabrication and continuous flow process for the benign-by-design nanomaterials synthesis, showcasing some selected examples of innovative biomaterials in the field of wastewater treatment and catalysis.

## INTRODUCTION

The interest and excitement in the field of biomaterials design and applications has been a hot topic in recent years. Biomaterials, original from either natural sources or synthetic polymers, exhibit a number of unique properties being also widely available, biocompatible and biodegradable for several applications in catalysis, wastewater treatment and biomedicine (1, 2). Up to now, various synthetic methodologies have been reported for biomaterials design which include spray-drying, precipitation polymerization, coacervation, emulsion crosslinking and microfluidics. With the rapid development of microfluidic technology, there is an opportunity to create active biomaterials with precisely controlled morphologies. However, the synthesis process always comes with changes in activity which can significantly influence their applications. For catalytic applications, the activity of a catalyst can be irreversibly reduced, potentially leading to deactivation. Comparably, the adsorption capacity can decrease in wastewater treatment. In this regard, an appropriate rational design and post-synthetic processes are employed with this purpose. Both chemical modifications and the incorporation of active phases can improve their properties and endow them with unlimited potential for wider applications.

The environmental footprint of anthropogenic activities (e.g. air and water pollution) has remarkably increased in recent years and evidenced in the direct discharge of untreated and partially treated wastewater containing complex contaminants into the environment (3). Heavy metals, which can be hardly biodegraded and gradually accumulate in aquatic environments, are among the most significant issues present in wastewater. Various methodologies including chemical precipitation, ion-exchange, electrochemical reaction, membrane filtration and adsorption have been developed from which adsorption represents the most promising considering factors such as the nature of wastewater (pollution concentration, pH, treatment throughput), investment costs, energy requirements and consumption, and emission standards (4, 5).

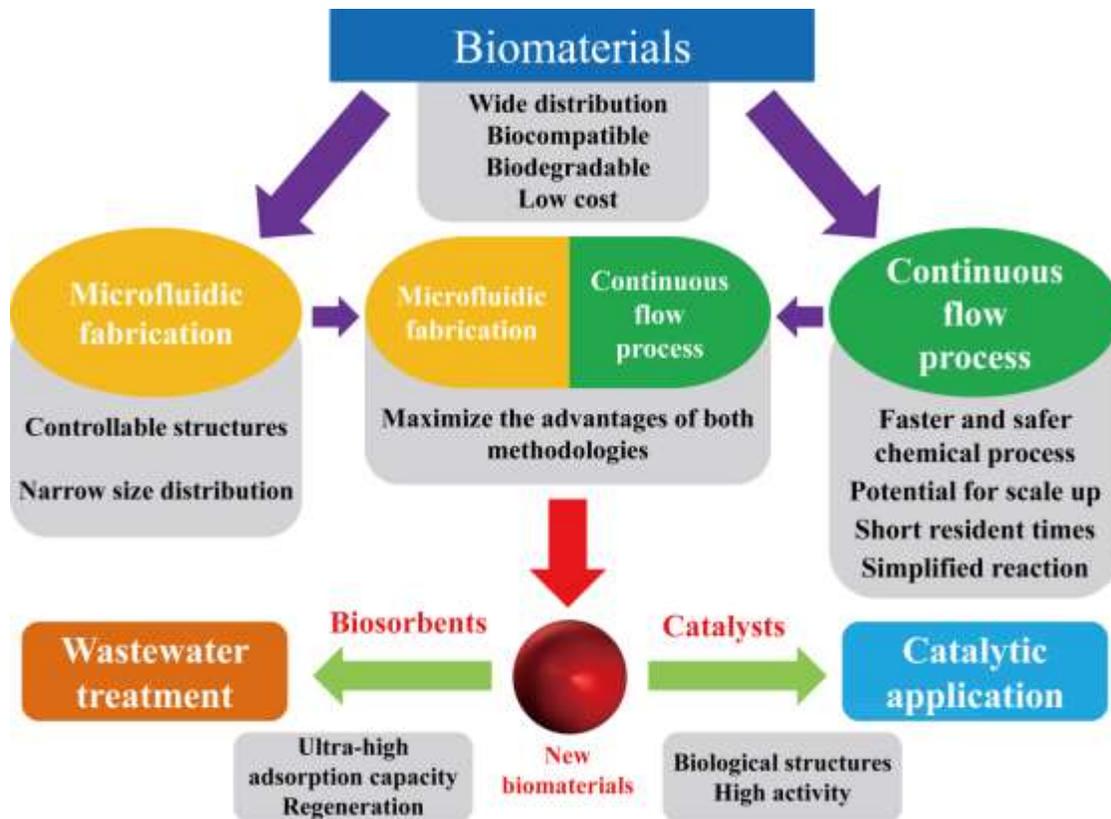
Natural biomaterials such as activated carbon, tobacco dust, macrofungus and montmorillonite are widely available at low cost, but they usually show unsatisfactory non-selective adsorption capacity and poor mechanical properties. Meanwhile, the

development of synthetic polymers has been thwarted by their cumbersome fabrication processes, with high cost and uncontrollable by-products, also resulting in secondary pollution. New biomaterials based on natural materials with facile and reliable targeted modification processes seem to be a promising alternative that can provide outstanding advantages of economy, efficiency, reliability and regeneration in wastewater treatment applications. In this regard, much attention has been recently paid to chitosan due to its natural characteristics. The combination of microfluidic fabrication and the possibility of including functional groups via grafting takes to the next step the adsorption capacity of chitosan microspheres.

Catalysis is a central concept in chemistry, playing, for instance, a key role in industrial processes both under homogeneous and heterogeneous conditions (6). In particular, the excellent properties of metal nanoparticles including high surface areas, large concentration of highly undercoordinated surface sites and the presence of quantum confinement effects have drastically altered their reactivity and make them promising heterogeneous catalysts. Among metals, Pd and Au are most effective catalysts for carbon – carbon bond formation (Pd) and variety of redox reactions (Au). However, supported nanoparticles can be only used at moderate to low temperature conditions due to their poor thermal stability which greatly limited their further industrial implementation. To fulfil this gap, the development of biomaterials with excellent features is of great interest (7), particularly under microfluidics which allows the possibility to design nanomaterials with narrow size distribution.

Continuous-flow processes as a highly efficient post synthesis procedure possess inherent advantages in terms of faster and intrinsic safer chemical processes, potential for scale up, short resident times and simplified reaction setups. In terms of improved activities and controllable processes, a batch reaction is far behind a continuous-flow process (8). The rate of heat transfer can be also increased by employing a highly conducting steel-based microfluidic set-up.

In view of the above premises, the areas of bio(nano)materials for various applications still have room for significant developments, particularly in their design using microfluidics and/or continuous-flow processes (Figure 1).



**Figure 1.** Benefits of the combination of microfluidic fabrication and continuous flow processes for the design of novel bio(nano)materials.

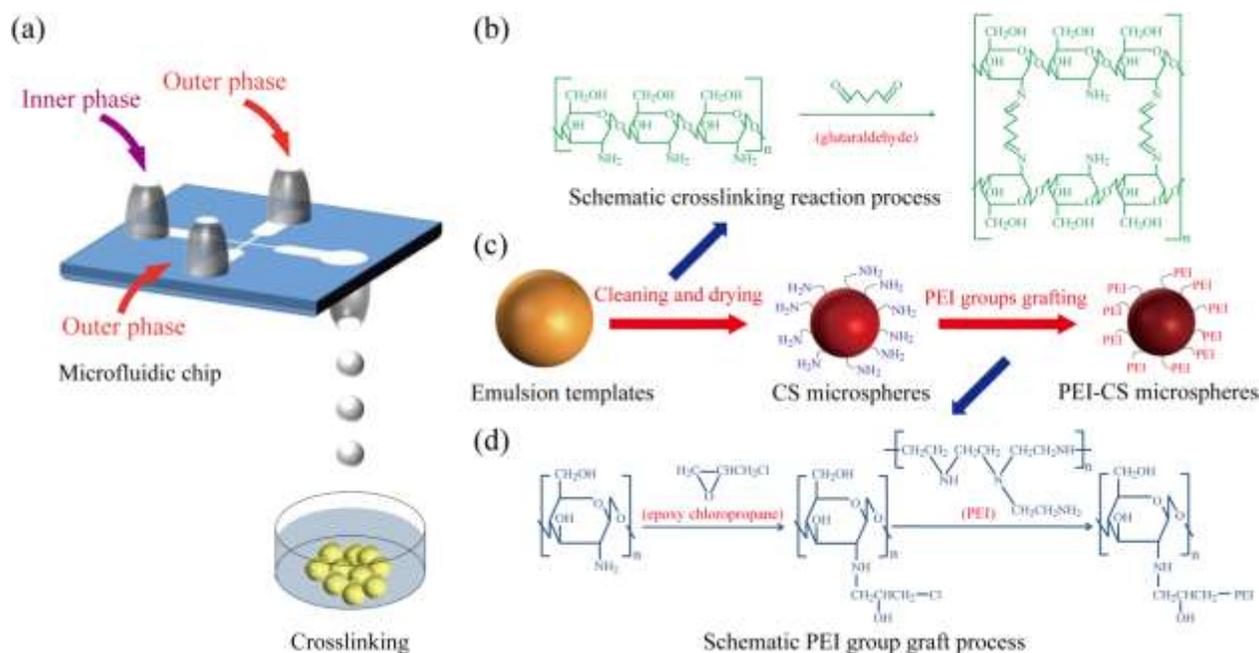
## WASTEWATER TREATMENT

Chitosan, originated from chitin deacetylation, is a unique alkaline polysaccharide ubiquitous in the natural world which exhibits excellent physicochemical properties being nontoxic, biocompatible and biodegradable (9). Importantly, the potential to functionalise chitosan is rather significant i.e., esterification, chelation, and graft copolymerization due to the presence of hydroxyl and amino groups in its structure. However, chitosan is known to be very sensitive to changes in pH as it can either form a gel or dissolve which hinders its practical applications (10). Developing chitosan microspheres as compared to its typical form (powders or flakes) can significantly improve its stability and convenience for recycling. Up to now, several chitosan microspheres fabrication methods have been reported including spray-drying, precipitation polymerization,

emulsion crosslinking, solvent extraction, membrane and microfluidic syntheses (11, 12). Microfluidically-synthesized chitosan microspheres with high monodispersity and controllable morphology have attracted a great deal of attention in water treatment (13). However, the final adsorption capacity of them depends on the amount of remaining amino groups which are gradually consumed in the crosslinking process.

A novel and highly versatile PEI-CS biomaterial was synthesized by an integrated process with facile microfluidic emulsion, chemical crosslinking, solvent extraction, and functional groups modification, as shown in Figure 2a and c. In our study, the microfluidic flow-focusing chip comprised three layers: the top layer (containing three inlet orifices with the same diameter, 2 mm), the middle layer (containing the flow-focusing junction), and the bottom layer (containing one enlarged outlet orifice with 4 mm diameter). The channel width at the flow-focusing junction was 1 mm and the broadened channel expanded to 2 mm to reduce pressure resistance and guarantee the smooth transportation for emulsion templates. We used Teflon tubes to connect our microfluidic flow-focusing chip with syringe pumps, with the outer phase and inner phase respectively injected into the microchip by two syringe pumps with different velocities at the same time. At the flow focusing junction, the inner phase was sheared by the outer phase to yield a series of highly monodispersed emulsion templates. Herein, in our study, the inner phase was an aqueous solution (4.0 wt% chitosan and 2.0 wt% acetic acid), while the outer phase was n-octanol with 2.0 wt% Span80. As-prepared emulsion templates were collected and crosslinked in a solidification bath, where the Schiff's base reaction took place on the interaction between glutaraldehyde (-CHO) and -NH<sub>2</sub> groups from chitosan (Figure 2b). Glutaraldehyde widely used for crosslinking served as the crosslinking agent while n-octanol served not only as inner phase, but also as an effective extractant for the emulsion templates. After crosslinking, the emulsion templates were thoroughly washed with acetone, alcohol and an excess of deionized water before final drying at 40 °C for 3 h. Figure 2d schematically depicts the follow polyamination process. As-prepared CS microspheres were placed into isopropyl alcohol with 0.5wt% epoxy chloropropane. The reaction was carried out at 50°C for 2h accompanied by gentle stirring, followed by washing and mixing in 30wt% polyethylenimine (PEI) aqueous solutions at 80 °C for 3h under continuous stirring. The

final product, PEI-CS microspheres, was washed with deionised water thoroughly and dried at 40°C for another 2h.



**Figure 2.** (a) Schematic synthesis process of CS microspheres; (b) Schematic cross linking reaction process; (c) Schematic chemical modification of PEI-CS microspheres; and (d) Schematic PEI group graft process.

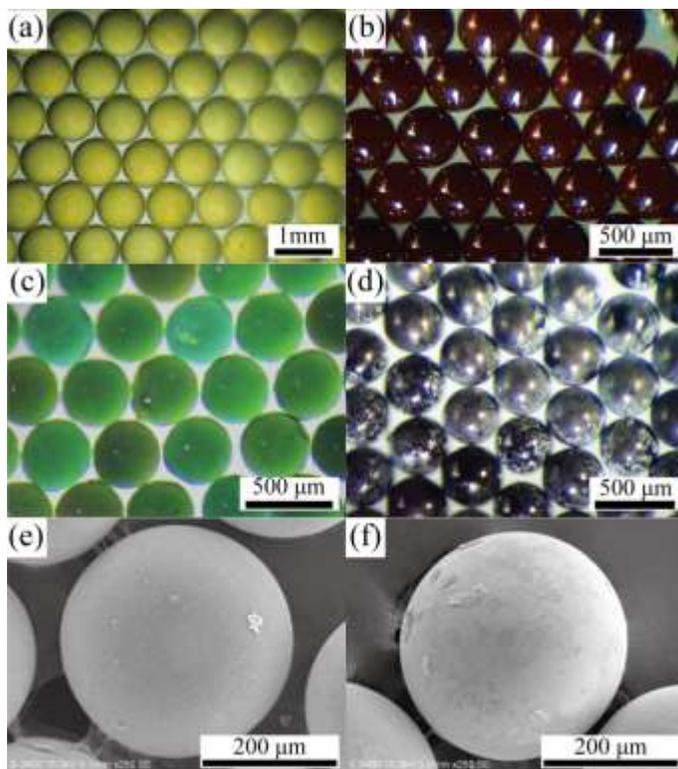
## RESULTS AND DISCUSSION

A precise size control of CS microspheres can be achieved by varying the weight percent of chitosan in the inner phase or the velocities of two phases. The average diameter of the emulsion templates was found to increase with an increase in the weight percent of chitosan and a decrease in the flow rate outer /inner phase ratio. In our study, the size of emulsion templates could be easily controlled in a wide range, from 990  $\mu\text{m}$  to 1522  $\mu\text{m}$ . n-octanol played an important role in the dimension control of CS microspheres as it extracts water from emulsion templates and causes a shrinkage in the final CS microspheres. The average diameter of synthesized PEI-CS microspheres

was 378  $\mu\text{m}$  (CV=2.3 %). Importantly, this CV value is comparatively reduced to that of other materials synthesized by conventional means, i.e., stirring or membrane (around 10%). This property is of great benefit for a high degree control over the microparticles due to the inherent advantages of the simple microfluidic technology.

In our study, PEI-CS microspheres were employed as a novel biosorbent for toxic heavy metal ions wastewater treatment. Amino groups have good affinity towards metal ions and can form stable metal chelates. Cu ions were chosen as model contaminant to study the adsorption properties of PEI-CS microspheres. Considering Cu ion hydrolysis in alkaline environments and protonation of amino groups in strong acid media, the subsequent adsorption experiments were performed under mild acidic aqueous conditions (pH=5.5) in duplicate. CS microspheres were also prepared and tested in the adsorption experiments for comparative purposes.

Optical micrograph images exhibited colour changes of microfluidically-synthesized materials at different stages (Figure 3a-d). The emulsion templates were golden yellow with cross-linking time 30 min as shown in Figure 3a. With an increase in the degree of crosslinking, the colour will deepen. After reaching adsorption equilibrium, CS microspheres (Figure 3b) turned dark green (Figure 3c) while a layer of light blue powder could be observed attached to the surface of PEI-CS microspheres (Figure 3d). Integrated with SEM images, it further demonstrated that both PEI-CS microspheres and CS microspheres are solid spherical structures as depicted in Figures 3e and f, containing some attached surface material.



**Figure 3.** Optical micrograph images of (a) chitosan emulsion templates with crosslinking 30 min; (b) CS microspheres (b) before and (c) after adsorption equilibrium; (d) PEI-CS microspheres after adsorption equilibrium; SEM images of (e) CS microspheres and (f) PEI-CS microspheres.

Adsorption kinetics and adsorption isotherm of CS and PEI-CS microspheres have been intuitively compared and systematically studied. As shown in Figure 4a, both the adsorption kinetics of CS and PEI-CS microspheres can be well fitted with pseudo-second order model, since their correlation coefficient ( $R^2$ ) are larger than 0.99. 144 h were needed to reach adsorption equilibrium for CS microspheres, with the final adsorption capacity of ca. 76 mg g<sup>-1</sup>, improved as compared to the largest literature reported value ca. 52 mg g<sup>-1</sup>. In comparison, PEI-CS microspheres exhibited an outstanding performance in adsorption kinetics (ca. 64 h to reach equilibrium) with an adsorption capacity of ca. 146 mg g<sup>-1</sup>. The Langmuir adsorption model could be used to well describe the whole adsorption process of both PEI-CS and CS microspheres (Figure 4b). The calculated adsorption capacities at adsorption balance were 157 mg g<sup>-1</sup>

for PEI-CS microspheres and  $80 \text{ mg g}^{-1}$  for CS ones, with  $R^2 = 0.990$  and  $0.998$ , respectively, in good agreement with practical adsorption values.

Mechanical properties of a material rely on the capacity to resist external pressure and remain physically unchanged, critical for adsorption and separation procedures.

Especially, mixers are widely used for homogeneous mixing process in industrial applications, while, hydrocyclones are convenient for rapid two-phase separation. If the adsorbents undergo any physical transformation/damage in either process, a significant contamination can be present in the system. 60 random samples of as-prepared PEI-CS microspheres with different crosslinking times were individually tested using a force gauge with continuous increasing force until microsphere rupture. The relationship between crosslinking time, mechanical strength and adsorption capacity of PEI-CS microspheres is depicted in Figure 4c. Mechanical strength of the biomaterials was obviously improved at increasing crosslinking time. After 60 min crosslinking time, the mechanical strength of PEI-CS microspheres reached  $0.368 \text{ MPa}$ , significantly superior to that of natural sorbent materials which normally need additional features in practical industrial processes, and even comparable to some commercial engineered polymers (polymeric ion exchange resin or ionic liquid gel,  $0.1 \text{ MPa} - 0.21 \text{ MPa}$ ). Additionally, the final adsorption capacity of PEI-CS was hardly affected in the crosslinking procedure.

In actual wastewater, the existence of other metal ions may poison the adsorption capacity of adsorbents. Sodium and aluminium ions, abundant in natural water source (*i.e.*, sea, river and mineral water) were also employed and added to copper solutions to study the selectivity of PEI-CS microspheres towards copper ions in the presence of contaminants. The selectivity towards copper ions reached a staggering  $94.7\%$ , improved as compared to CS ( $86.8\%$  at the same initial concentration of copper) in the presence of  $400 \text{ ppm}$  sodium and aluminium (Fig.4d). Even decreasing the concentration of copper ions down to  $100 \text{ ppm}$ , an  $83\%$  selectivity towards Cu ions was achieved for PEI-CS microspheres, unprecedented in literature.

The readsorption efficiency ( $R_E$ ) and readsorption capacity was also measured to investigate the regeneration performance of PEI-CS microspheres, as focus of industrial adsorption application. In our study, a NaOH solution containing  $1.5 \text{ wt}\%$  ethylene diamine tetraacetic acid (EDTA) was utilized as desorption solution. We found that

NaOH concentration had a great influence on readsorption capacity, showing a minimum of 48.6% within 3 cycles at NaOH concentrations of 0.5 mol L<sup>-1</sup> (Figure 4e). The readsorption capacity under these conditions (Figure 4f) was only 83 mg g<sup>-1</sup>, almost half of the initial adsorption capacity. These results pointed out that PEI groups will be consumed under a strong alkaline environment. In this regard, we reduced half of the NaOH concentration and obtained an acceptable regeneration property, with an  $R_E$  larger than 71.2% after 5 adsorption-desorption cycles.

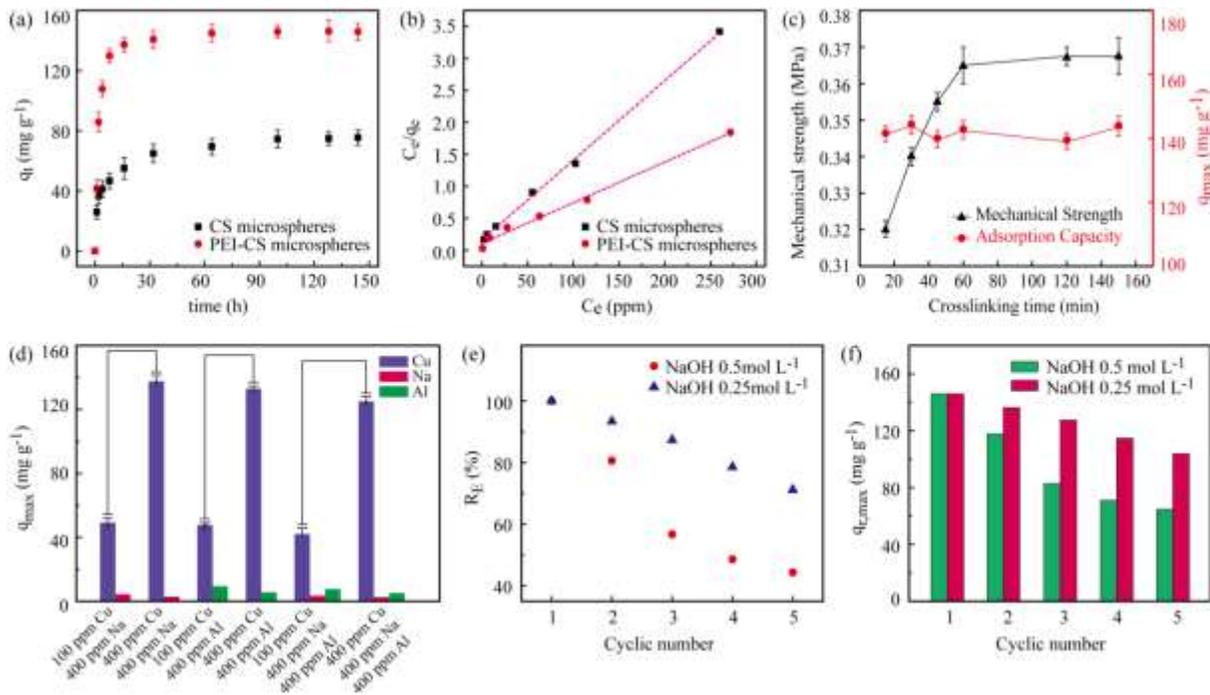


Figure 4. (a) The adsorption kinetics and (b) The linear fitting curves of Langmuir equation of the adsorption isotherms of PEI-CS microspheres and CS microspheres; (c) The relationship of crosslinking time, mechanical strength, and adsorption capacity of PEI-CS microspheres. (d) Selective adsorption; (e)  $R_E$  and (f) maximum readsorbance of PEI-CS microspheres for 5 adsorption-desorption cycles.

## CATALYTIC APPLICATIONS

Nanomaterials featuring wide availability, biocompatibility and low cost emerged as a popular source to synthesize high added value chemicals, fuels and functional materials (1). Furfural as a highly useful chemical intermediate can be converted into different high added value chemicals and fuel precursors including furfuryl alcohol (FA), 2-methylfuran (2-MF), 2-methyltetrahydrofuran (2-MTHF), and cyclopentanone (CPO) by employing a number of homogeneous and heterogeneous catalytic systems (14). Although the pathways and reactivity of nanomaterials have attracted a significant deal of research efforts in the past few years, various processes still lack of valuable insights into reaction mechanisms and kinetics. Moreover, most research has been performed at moderate or even high temperatures, resulting in low practicality and applicability.

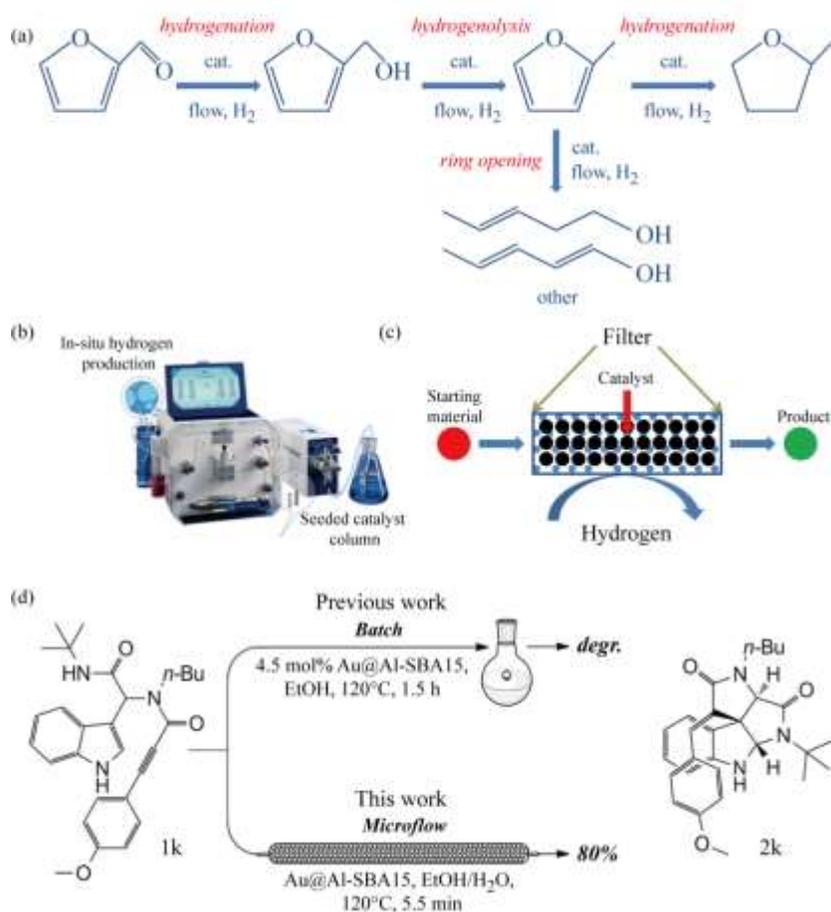
In order to offset this research gap and provide a better understanding of the reaction pathways and mechanisms of furfural conversion, as well as conversion selectivity, different commercial catalytic systems (i.e. noble vs. transition metals; homogeneous vs. heterogeneous) have been utilized and compared under continuous flow liquid phase conditions. More importantly, the stability of catalysts under typical biomass conversion conditions was also tested.

### **Development of novel nanomaterials for continuous flow hydroconversion of furfural**

Continuous flow hydrogenation reactions were performed in an H-Cube mini flow hydrogenation device showing in Figure 5b. Pure methanol, serving as the washing solvent, was firstly pumped into this system with the average flow of  $0.3 \text{ mL min}^{-1}$  for 15 min. Subsequently, methanol was replaced with an ethyl acetate solution ( $0.3 \text{ mL min}^{-1}$ , 10 min) under the optimum reaction conditions, where the reaction temperature was  $90 \text{ }^\circ\text{C}$  and hydrogen pressure was 50 bar. When reach the specify condition, a 0.2 M furfural solution in ethyl acetate was pumped into the system for the continuous flow hydroconversion of furfural. In this system, the flow solution passes through a packed column containing different solid catalysts and interacted with enough hydrogen original from water electrolysis, showing in Figure 5c. It is worth mentioning that furfural was serving as the starting material and the furfural solution was filtered before utilization to eliminate the residually undissolved species. Figure 5a depicts continuous flow

hydroconversion schematic. As the reaction proceeds, a fixed volume of samples were withdrawn at different time intervals and analysed. Besides, the catalyst deactivation should be monitored with time under the investigated reaction conditions. After the continuous flow process, ethyl acetate solution ( $0.3 \text{ mL min}^{-1}$ , 10 min) was introduced into the system again for unreacted furfural species and/or different products of the reaction removal before the final wash process with excess methanol ( $0.3 \text{ mL min}^{-1}$ , 20 min).

The results show that facile conversion of furfural to valuable chemicals can benefit from continuous flow hydrogenation processes. Pd catalysts provide optimum conversion results to 2-MF and even pentenols. Besides, we also found that the Pd loading degree and the oxidation states of Pd species in the catalyst give reasonable explanations to mechanistic aspects and deactivation pathways. In our study, 5% Ru/C was selected as optimum alternative for high FA yields. Comparably, transition metal catalysts were proved to show moderate yields and varying selectivity to products (mostly to FA) in the flow conversion of furfural under optimum conditions. The deactivation of catalysts was inevitable in this process. In this regard, we believe our study propose significant guidelines for the design of more stable catalytic systems for the continuous flow hydroconversion of other platform chemicals (e.g. succinic and lactic acids, sorbitol).



**Figure 5.** (a) Schematic continuous flow hydroconversion of furfural using heterogeneous catalysts; (b) Flow hydroconversion of furfural using an H-Cube mini system; (c) Continuous flow conversion of furfural (starting material) to products over a packed bed of heterogeneous catalysts in the H-Cube mini system; (d) Comparison of the gold-catalysed spirocyclisation of challenging Ugi-adducts in batch and continuous flow with a packed-bed reactor.

### Development of novel nanomaterials for the cycloisomerisation of Ugi-adducts

Gold nanoparticles have been extensively utilised as homogeneous and heterogeneous catalysts. Under homogeneous catalytic conditions, gold catalysis exhibited a unique reactive performance for synthetic transformations even under mild reaction conditions (15). However, in terms of cost, productivity, robustness and environmental sustainability, gold-catalysed processes for industrial applications are still in their infancy.

Especially, the application of heterogeneous gold catalysts has been greatly limited by high temperature operating conditions. In this regard, the best solution to these problems is continuous-flow process using highly active supported gold nanoparticles in a packed-bed reactor (16). Compared to traditional batch processes, the combination of heterogeneous gold catalysis with microflow reactor technology displays unparalleled advantages, including enhanced mixing, improved heat transfer, increased selectivity and safer reaction conditions. Additionally, it is also convenient for catalyst reuse with less impurities in the final product.

Recently, a novel heterogeneous gold catalyst, Au@Al-SBA15, for the cycloisomerisation of Ugi-adducts to obtain various spiroindolines and diazepino[1,2-b] in diazoles by integrating the efficient continuous microflow approach (17). In detail, the heterogeneous gold catalyst Au@Al-SBA15 was first prepared by ball-milling process under the optimized milling conditions, 10 min milling at 350 rpm (18), followed by calcination at 400 °C, 4 h under air. As a result, a large amount of Au nanoparticles can be homogeneously distributed on the surface of the support rather than inside the pores of the material. This outstanding structural property endows the final heterogeneous gold catalyst with increased catalytic activity and narrower diameter range.

The gold-catalysed spirocyclisation reaction of Ugi-adducts was performed in a stainless steel packed bed microreactor filled with as-prepared gold catalyst Au@Al-SBA15 (19), showed in Figure 5d. The reaction was conducted at 120 °C and a pressure of ca.10 bar. In general, one reactor filling could be used for up to 8 reaction cycles.

In comparison with conventional batch condition, excellent yields and improved conversion could be easily achieved under microflow conditions since the ratio of catalyst to reactant is much higher in the packed bed reactor. However, under continuous microflow conditions, as-prepared catalysts exhibited unsatisfactory reusability as its activity significantly declined after eight reaction cycles. Integrating ICP-OES, XPS, and TEM measurements, two reasonable explanations could be provided, related to: (i) oxidation of Au (0) to Au (III) and (ii) agglomeration of the nanoparticles.

## **CONCLUSIONS AND OUTLOOK**

The potential of bio(nano)materials has been exemplified in numerous applications, with however inherent disadvantages including unsatisfactory adsorption capacity, poor mechanical strength and unacceptable catalytic activity that have greatly limited their applications. The discovery of microfluidically-synthesized bio(nano)materials and applications in continuous flow processes has opened up great opportunities for adsorption and catalytic applications since the precisely tailored structure not only enhanced the mass selective transfer and exchange, but also offered additional possibilities for catalytic reactions, while preserving the intrinsic properties of bio(nano)materials. The selected example, PEI-CS microspheres, clearly highlights the usefulness and significance of the development of microfluidic-synthesized biomaterials for wastewater treatment. Another significant advancement in flow chemistry research is the use of novel continuous-flow process which not only provides faster and safer chemical process with short resident times, but also greatly improves the activity and controllability of bio(nano)materials for catalytic applications. Although we witness the rapid and lasting development of both the microfluidic fabrication and continuous flow process as well as their outstanding performances in their own applications, the combination of them have been rarely seen. The application and potential of new bio(nano)materials obtained by an integrated protocol of microfluidic fabrication and continuous flow process is virtually unlimited. We believe these preliminary results can provide an useful guidance for novel biomaterials fabrication and greatly revolutionize the newly designed biomaterials in efficient wastewater treatment and promising catalysis applications in the future.

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