Chapter

Microfluidic Synthesis of Functional Materials as Potential Sorbents for Water Remediation and Resource Recovery

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Abstract

The advance of droplet-based microfluidics has enabled compartmentalization and controlled manipulation of monodispersed emulsions with high yield and incorporation efficiency. It has become a highly exotic platform in synthesizing functional material due to the presence of two immiscible liquids and the interface between them. With its intrinsic feature in high degree of product control, advanced emulsion-based synthesis of functional material is constituted as a template for effective water remediation and resource recovery. This chapter aims to provide an overview of recent advances in microfluidic technology for environmental remediation. More specifically, the facility of microemulsion-based functional materials for water remediation is reviewed. Moreover, the removal and recovery of pollutants, such as heavy metal, dye, pharmaceuticals, etc., from aquatic environment by the applications of adsorption on functional micro/nanomaterials are unfolded with respect to its potential for wastewater purification.

Keywords: microfluidics, remediation, functional sorbents, recovery, wastewater

1. Introduction

Over the past few years, tremendous growth in the manufacturing and widespread application of synthetic chemical compounds in industrial sectors has led to growing number of emerging contaminants in environmental matrices (air, wastewater, water, sediment, and soil), which poses a challenge for regulatory agencies. Apart from that, the environment has gradually suffered as a result of exposure to the emerging pollutants especially in water and wastewater. Various types of physical, chemical, and biochemical methodologies have been reported on effectively removing pollutants. These methods include membrane separation, biological degradation, advanced oxidation process, and adsorption as well [1]. Recent developments have indicated that the adsorption method is favorable due to its wide availability, lower cost, as well as its recyclability. As in terms of cost effectiveness, simplicity of construction, and easy adaptation of operating conditions, particle adsorption materials become the key for realizing various adsorption applications in environment remediation using fixed bed reactors, absorption columns, fluidized beds, and cyclone separators [2]. However, controlled shapes, size, and compartments are some of limitations for most conventional methods. Unlike conventional approaches, microfluidics is comparably conducive as it has improved and extended the possibilities to synthesize highly controlled size of microparticles with excellent adsorption capability and reusability [2].

Microfluidics is a multidisciplinary field stretch across engineering, physics, chemistry, microtechnology, and biotechnology. Microfluidic devices generally have two of the three geometric length scales in the order of microns. The micrometer length scale defines the most obvious but extremely important character of microfluidic devices especially their small size, which allows small sample volumes, low cost, and fast analysis, but with high resolution and sensitivity [3]. With the length scale associated with microfluidic devices, the flow within them tends to be laminar. Moreover, one characteristic of microscale miniaturization is the large surface area to volume ratio. Thus, this favorable aspect plays a major role in control and manipulation of fluid flow in microfluidics. Recent advances and innovations could make microfluidics technology ubiquitous and create microfluidic devices that are more functional, efficient, and cost effective than conventional techniques.

The development of microfluidic systems that allow for the formation of microdroplets inside microfluidic devices has gained greatly attention over the past 20 years. The rise in interest is due to the utilization of microfluidic devices in a broad range of biological and biomedical application areas including disease diagnosis, cell treatment, drug screening, single-cell analysis, and drug delivery. Liquid droplets dispersed in a second immiscible fluid are useful, particularly when the sizes and the size distribution of droplet can be prescribed on a few hundred nanometers to a few millimeters [4]. Microfluidic emulsification approach offers an alternate and versatile route to produce emulsions that are highly monodispersed and have high formation frequencies in multiphase fluid systems [5]. Additionally, the geometrical attributes and flow characteristics within these microfluidics system constitutes flexibility in producing complex structured emulsions, such as double-emulsions and multi-emulsions [6, 7]. Highly monodispersed single, double, or multi-emulsions can be used as a template to prepare micro- and nanoparticles with various structures and morphologies [7], as shown in **Figure 1**. As seen in **Figure 1**, the presence of different particle shapes, compartments, and microstructures is formed based on the flow and geometrical attributes in microfluidics. Consequently, the superior properties of droplet-based microfluidic device have become extremely promising and attractive platform that enables the production of functionalized monodisperse microparticles.

In order to fabricate micro- or nanoparticles, the analysis of droplet formation is imperative to understand the device operation and its process control to meet different application purposes. Additionally, other's droplet manipulation, such as fusion, fission, mixing, and sorting with high precision and flexibility constitutes essential issue, at which extensive investigations have been directed. Based on the sources of the driving force involved, there are five approaches to droplet manipulation: hydrodynamic stress, electro-hydrodynamics, thermos-capillary, magnetism, and acoustics [8]. Hydrodynamic stress is a simple and effective approach to accomplish droplet manipulation relating to the geometrical characteristics of microchannel [9]. In this mode of manipulation, various methods have been employed in the formation of droplets in microfluidics device, including co-flowing mechanisms, flow-focusing mechanisms as well as cross-flowing mechanisms [10]. These mechanisms enabled the formation of dispersions with highly attractive features, particularly the control over droplet and particle size distribution.

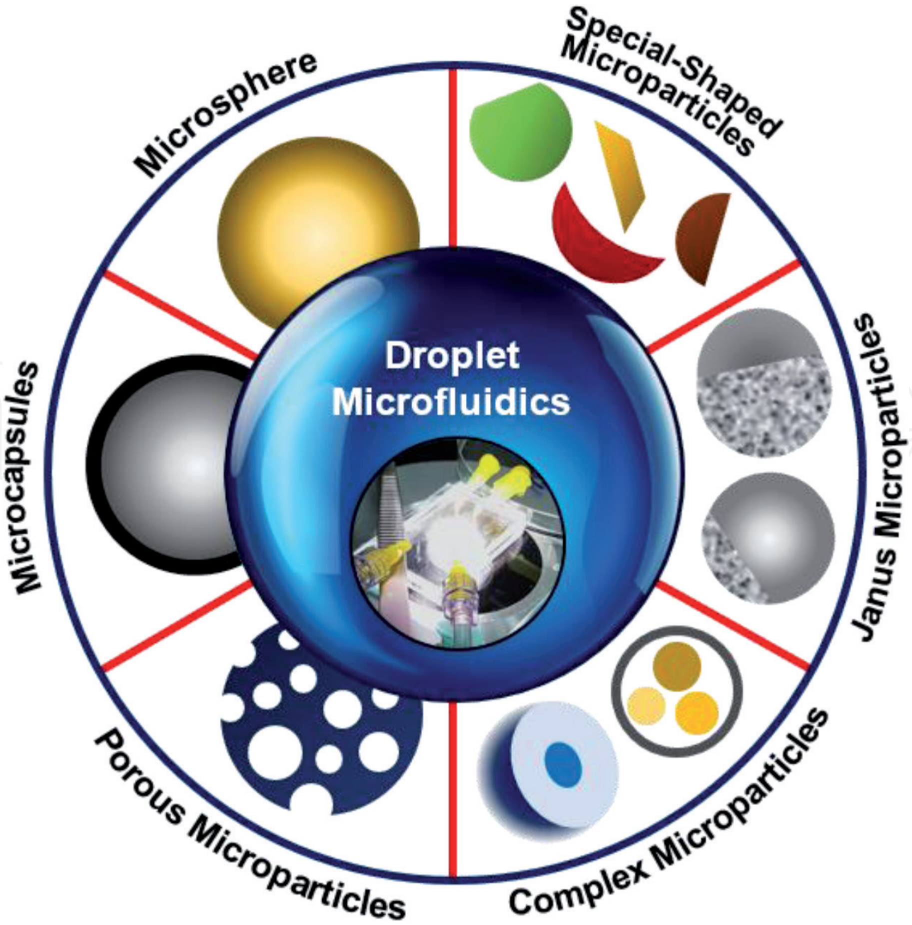

Figure 1.
Classification of various structures of microparticles produced by droplet-based microfluidics.

Over the years, microfluidic devices have been developed to synthesize particles for water remediation. For instance, Zhao et al. [11] synthesize graphene oxide microspheres using microfluidics technology for the removal of perfluorooctane sulfonate. Dong et al. studied the anionic dye adsorption using chitosan microparticles [2]. In addition, the performance of microcapsules for the CO_2 adsorption and permeability was investigated by Stolaroff et al. [12]. Hitherto, there are still little attempts that have been considered to use microfluidic platform as a selection scheme for large-scale industrial wastewater treatment. Toward practical and high capacity, microfluidic platforms generally suffer from the high cost and limited capacity for high throughput production of microfluidic synthesized particles. Nevertheless, it is possible to operate the production in parallel in order to realize continuous processes [13]. Moreover, the fundamental microfluidic research is still highly demanded to bridge the gap between the functional material synthesis and industrial perspective on exploring the possibilities and potential benefits of microfluidic processes [2, 13].

In this chapter, we will discuss the current trend of employing microfluidic technologies for environmental remediation, specifically for wastewater treatment and water remediation. Apart from that, we will also provide a general overview of the facility of microfluidics emulsification for the fabrication of various microparticles and nanoparticles as functional adsorbents. The sorption capacity and performance of the functional materials will be also evaluated in this review. Eventually, this chapter provides an impression of what are the consolidated fields of microfluidic formulation in functional material synthesis that will look like in about a decade from now.

2. Microfluidic technology for water remediation and resource recovery

Due to excessive discharges of harmful wastes and by-products to the environment, water contamination is the most prominent in which numerous organic and inorganic pollutants are found in the fresh water resources such as ponds, rivers, and underground water. Traditionally, there are various methods of water analysis including atomic adsorption, chemical analysis, chromatography, colorimetry, and spectrometry. Although these techniques have high sensitivity and accuracy, limitations such as expensive instrumentation, time consuming and requires manual operation in sampling process, causing the researchers to shift their interest toward microfluidics technology, which has a great potential to replace the traditional water analysis techniques [14].

2.1 Droplet microfluidic system

Droplet-based microfluidic technology involves the formation and manipulation of discrete droplets inside microdevices [15]. Droplet microfluidics is being widely used in different applications, such as chemical reactions, therapeutic agent delivery, imaging, biomolecule synthesis, diagnostic chips, and drug delivery [16]. The major concerns when creating droplet microfluidic device are the type of microfluidic chip fabrication materials used and the fluids used for droplet generation. Poly(dimethyl)siloxane (PDMS) is commonly used as fabrication material of microfluidic devices because PDMS is a relatively low cost and easily moldable elastomer. Nevertheless, PDMS has low solvent resistance, causing it to deform in the presence of strong organic solvents. Therefore, materials with higher solvent resistance, such as glass [17] and silicon, [18] are used. The pros and cons of the application of different microfluidic chip materials in droplet microfluidic system are shown in **Table 1**. The application of droplet microfluidics in the formation of functional materials for removal of pollutants will be discussed in Section 3 subsequently.

2.2 Microfluidic reactors

Microfluidic reactors, also known as microreactors, have been widely used in wastewater treatment because the development of microfluidics technology in this area helps to overcome some existing problems in bulk reactors. The two essential issues of bulk reactor are photon transfer limitations and mass transfer limitations [20]. Thus, great attention and interest have been shown in microfluidic system as microreactor inherits the merit of microfluidics. Recently, the technologies of microfluidics in advanced oxidation processes (AOPs) for wastewater treatment were studied and focused. AOPs involve the utilization

Application	Glass/ silicon	Elastomers	Thermoset	Thermoplastics	Hydrogel	Paper
Droplets formation	Excellent	Moderate	Good	Good	N/A	N/A
Production cost	High	Medium	High	Low	Medium to high	Low
Reusability	Yes	No	Yes	Yes	No	No

Table 1.
Pros and cons of different microfluidic chip materials for different applications [19].

of hydroxyl radicals ($OH^{\cdot}$) or sulfate radicals ($SO_4^{\cdot -}$) as a major oxidizing agent to effect water purification [21]. This is because these powerful radicals are extremely effective to destruct the organic and inorganic contaminants in wastewater and transform them to less or even non-toxic products [22]. The most popular AOPs that employ the technologies of microfluidics are photocatalysis and Fenton processes. The development and application of several AOP mechanisms will be discussed in the next sub-section. Then, a brief example of the application of different types of microreactors in water treatment and resource recovery is listed in **Table 2**.

2.2.1 Photocatalysis

Heterogenous photoassisted catalysis, known as photocatalysis is one of the examples of hydroxyl radical-based AOPs which is of particular concern in wastewater treatment. It involves the utilization of light for decomposition or mineralization of organic pollutants into innocuous product, such as carbon dioxide and water, in the presence of catalysts [31]. The application of microfluidic technology offers a great number of advantages in photocatalytic water treatment. Microfluidic structures have larger surface-area-to-volume ratio, typically in the range of 10,000–50,000 m^2/m^3 [32], compared to bulk reactor in which the surface-area-to-volume ratio is typically below 600 m^2/m^3 [33]. The surface-area-to-volume ratio can be much larger if nanoporous photocatalyst

Microfluidic device design	Application	Result	Ref.
Optofluidic planar reactor	Degradation of methylene blue	30% of dye degraded within 5 min with a reaction rate constant two orders higher than bulk reactor	[23]
Microcapillary reactor	Reduction of methylene blue	Reduction rate of dye increased by >150 times compared to batch system	[24]
Tree-branched centimeter-scale reactor	Degradation of volatile organic compounds	95% of pollutants (benzene, toluene, ethylbenzene, m-p xylenes and o-xylene) degraded in <5 s of residence time	[25]
Jet-aerated microfluidic flow-through reactor	Degradation of clopyralid as model organic pollutant	Clopyralid is eliminated effectively after 1 hour under several conditions	[26]
Microfluidic atmospheric-pressure plasma reactor	Degradation of methylene blue	>97% of dye degraded	[27]
Droplet microfluidic reactor	Extraction of lead (II)	Pb (II) ion was selectively and completely removed from the simulated wastewater effluent within 2.00 s	[28]
Microfluidic chip with polymethyl methacrylate (PMMA) plates	Adsorption of copper (II)	Adsorption capacity of 42.08 mg/g is achieved	[29]
Simple cross microchannel microfluidic device	Quantification of bacterial cells in potable water	Bacteria were accurately enumerated within 15 min after fluorescent staining	[30]

Table 2.
Application of microfluidic technology in water remediation and resource recovery.

film is used. Thus, higher heat transfer performance can be achieved by using microreactors. Furthermore, the rate of reaction is significantly increased and consequently favors having higher throughputs [34]. With the enhancement of reaction rate, the reaction time is reduced. The time taken for degradation process in a microreactor takes only several to tens of seconds [35], whereas bulk reactor requires several hours [36]. Besides, microfluidic layer has short diffusion length, typically 10–100 μm to ease the diffusion of organic pollutants to the reaction surface [31]. In addition, microreactors usually contain an immobilized photocatalyst film under the thin layer of fluid. This can ensure a uniform irradiation on the reaction surface, resulting in higher photon efficiency [37]. Microreactor has self-refreshing effect as the running fluid can refresh the reaction surface naturally. This helps to move away the reaction products and stabilize the photocatalysts. According to journal by Wang et al. [35], the photocatalysts in microreactor can hold several hundred runs of photocatalytic reactions, whereas the activity of photocatalysts in bulk reactors starts to degrade after 10 runs of reactions [38].

2.2.2 Other mechanisms in AOPs

Electro-Fenton process is an efficient AOP that involves activation of hydrogen peroxide by metal salts, typically iron, to produce hydroxyl radicals [39]. Electro-Fenton process is extremely effective in water remediation of the effluents, which cannot be efficiently treated using biological technologies [39–41]. Besides, AOPs with plasma-based water treatment (PWT) have been widely studied as PWT have the potential to reduce organic contaminants in wastewater. The application of microfluidic technology in PWT gives the benefits of large surface-area-to-volume ratio and flow control, in low-cost and portable devices [27]. However, more researches and development are needed to validate PWT performance at macro-scale [42].

3. Droplet microfluidics for the production of micro- or nanofunctional sorbents

Droplet-based microfluidics is formed through fabricating emulsions of uniform size. There are two approaches to produce emulsions, which are active and passive. Unlike actively controlled microfluidic devices, the breakup of discrete phase in continuous phase driven is controlled in a fully passive manner, which is caused by flow instabilities and hydrodynamic pressure without external actuations, such as mechanical, electrical, thermal, and magnetic method [43]. In this section, passive formation of emulsion-based microparticles is mainly discussed. Emulsions can be produced and manipulated with micro device of different geometries forming different sizes and morphologies [44]. Monodisperse emulsions are produced in laminar flow region and generated drop-by-drop where the over size, shape, and morphologies of micro droplets can be control precisely [45].

The superior properties of droplet microfluidics are advantageous for precise microparticle manufacturing for wastewater treatment. Micro and nanofunctional particles with various morphologies are prepared using templates. In general, microfluidic device forms highly monodisperse emulsified droplets and forms microparticles via solidification, while nanoparticles are formed using photochemical, chemicals or physical methods [46]. The space structure of the emulsions is controlled while preparing the adsorbent with microfluidic devices. By changing the device structure of microfluidic device, complex structure of droplets can be produced such as single, double, and multiple emulsion [17, 47]. These emulsion droplets are classified according to the structures and the evolvement of the emulsion into different structures and morphologies. Single emulsion can be a template to solid particles including spheres and non-spheres, while double and multiple emulsions can be templates for Janus particles, microcapsules, vesicles, hollow spheres or core-shell spheres [48].

3.1 Emulsion template: single, double or multiple

Single emulsions are droplets of one phase fluid dispersed in another immiscible phase fluid. Flow focusing, cross-flow, co-flow are systems that are frequently

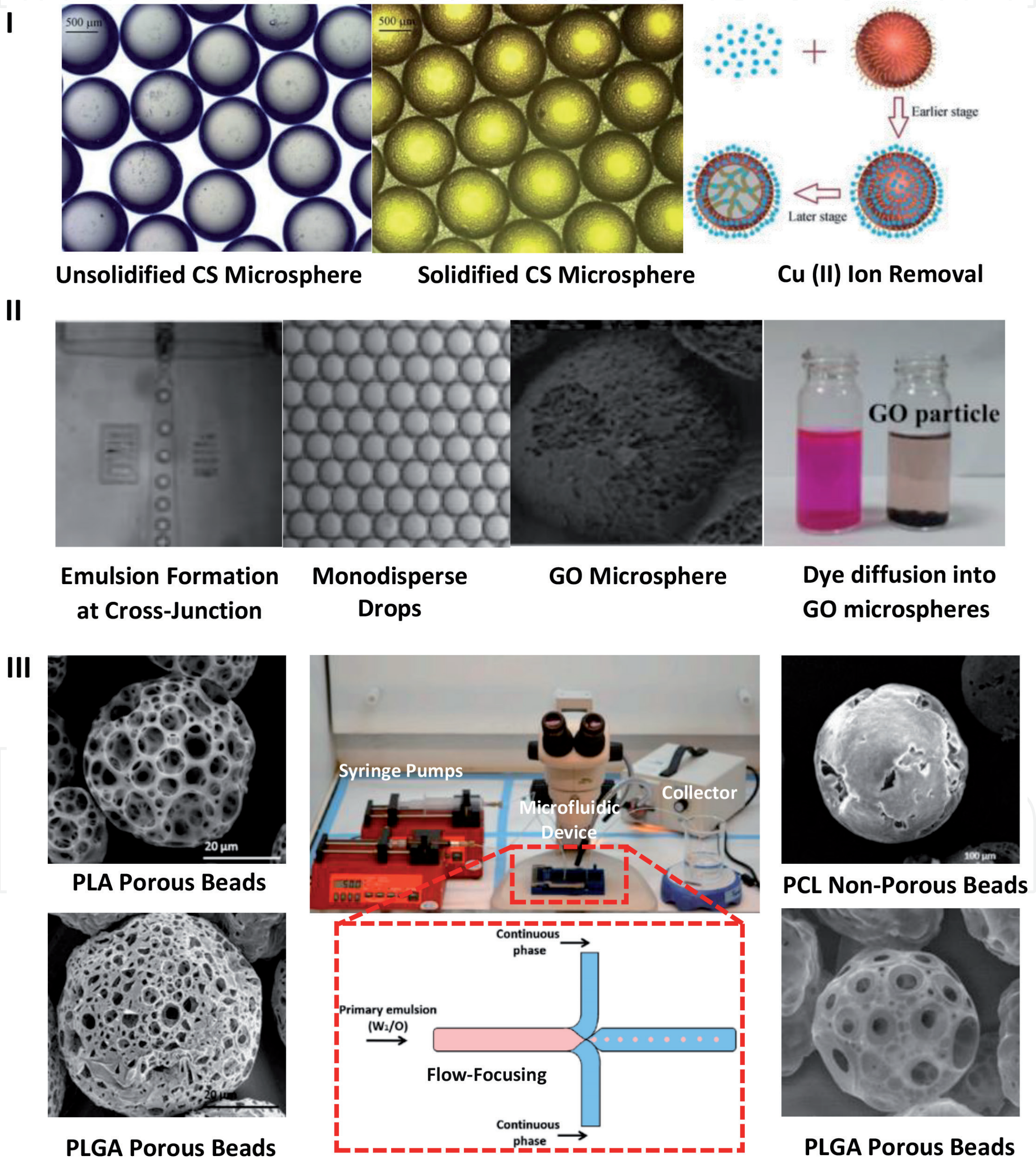

Figure 2.
Wastewater treatment by adsorption method onto microfluidic synthesized microparticles. (I) The adsorption process of heavy metal copper (II) ions using solidified chitosan microspheres (CS-MS) synthesized via cross-flowing PMMA-based microfluidics [29]. (II) Absorption of fluorescent dye molecules using PEGDA-graphene oxide (GO) microspheres [11]. (III) Microfluidic-based synthesis of porous and non-porous PLA, PLGA, and PCL microspheres [54]. (I) is reproduced with permission from Zhu et al., 2017, Copyright 2017, Springer Nature. (II) is reproduced with permission from Zhao et al. [11], Copyright 2016, Springer Nature. (III) is reproduced with permission from Amoyav and Benny [54], Copyright 2019, MDPI.

Microsorbent	Device	Approach	Channel size	Emulsion solidification	Ref.
Chitosan/polyethylenimine-chitosan microspheres	Commercial membrane	Membrane emulsification	Dispersed: 20 µm pores	Chemical cross-linking, solvent extraction	[55]
Chitosan/chitosan-poly(acrylic acid) composite microspheres	PMMA plates (laser fabrication)	Flow-focusing	Dispersed: 160 µm wide Continuous: 500 µm width	Chemical cross-linking, solvent extraction	[56]
Chitosan microspheres	PMMA plates (laser fabrication)	Cross-flowing	Dispersed: 1000 µm wide Continuous: 1000 µm width	Chemical cross-linking, solvent extraction	[29]
Chitosan microsphere	PMMA plates (laser fabrication)	Cross-flowing	Dispersed: 1000 µm width Continuous: 1000 µm width	Chemical cross-linking	[57]
Chitosan microparticles	PMMA plates (laser fabrication)	Flow-focusing	Dispersed: 500 µm width Continuous: 500 µm width	Chemical cross-linking	[2]
Thiourea-modified chitosan	PMMA plates (laser fabrication)	Flow-focusing	Dispersed: 160 µm width Continuous: 500 µm width	Chemical cross-linking, solvent extraction	[58]
Ion-imprinted chitosan microspheres	PMMA plates (laser fabrication)	Cross-flowing	Dispersed: 1000 µm width Continuous: 1000 µm width	Chemical cross-linking	[59]
Chitosan/silica hybrid microspheres	PMMA plates (laser fabrication)	Cross-flowing	Dispersed: 1000 µm width Continuous: 1000 µm width	Chemical cross-linking	[60]
Graphene oxide/$MgCl_2$-graphene oxide microspheres	PDMS chip (soft-lithography)	Cross-flowing	Not available	Photo-polymerization	[11]
Carbon nanotube microspheres	PDMS chip (3D printing/soft-lithography)	Flow-focusing	Dispersed/Continuous: 900 µm width with a downstream constriction: 200 µm width	Decanting, solvent, cleaning, drying, pyrolysis	[61]
Hollow silica microspheres with ethyl butyrate	Glass microfluidic chip	Flow-focusing	Dispersed/continuous: 250 µm width	Hydrolyzation and condensation	[62]
PDMS microspheres	Off-the-shelf (needle-based) microfluidics	Flow-focusing	Dispersed: 510 µm width with downstream channel: 600 µm width	Photo-polymerization	[63]

Table 3.
Microfluidic synthesized spherical and functional microsorbents for water remediation and resource recovery.

used to form monodisperse droplets, and the coefficient of variation of droplets is usually less than 5% [3]. There are five breaking modes in passive generation, which are squeezing, dripping, jetting, tip-streaming, and tip-multi-breaking. These five modes have its own characteristics, for example, the structure and component of the droplets can be changed to produce inorganic nanoparticles, metal particles, and polymer particles [49]. Double or multi-emulsions are droplets with smaller droplets encapsulated in larger drops [48]. These emulsions are produced with capillary micro devices that involve three fluid streams in different capillaries. Initially, single droplets are formed when inner fluid is sheared by the middle fluid, then double or multiple droplets are formed when the outer fluid pinched off the single droplets containing in the middle fluid. There are difficulties of precisely controlling the shell thickness, aggregation, and secondary nucleation.

3.1.1 Special-shaped particles

Non-spherical particles have unique properties, and they are usually fabricated with many strategies such as seeded emulsion polymerization [50], template molding [51], and self-assembly [52]. However, a high quality, monodisperse, non-spherical particles with tailored geometries and shapes yet still difficult to produce using these methods. Droplets with different sizes and shapes in microfluidic channels are confined with microfluidic technologies for fabrication of non-spherical particles. The droplet will be deformed into ellipsoid, a disk, or a rod if the largest sphere can accommodate in the channel of a larger volume of droplet. Non-spherical droplet will be formed after they are solidified in the confined channel [53].

3.1.2 Spherical particles

There are different types of spherical particles, such as polymer microspheres, inorganic microspheres, noble metal nanospheres, and semiconductor nanospheres [48]. Polymer microspheres are usually prepared through spray-drying, coacervation, and emulsification [48]. Inorganic microsphere, which is the composed of titanium, silica, and carbon, have potential application in biomolecules, sensor, catalyst, and drug deliver. Noble metal nanosphere, such as gold, silver, and platinum, has shape and size dependent properties. It is hard to obtain desired size and size distribution as this individual nanoparticle tends to precipitate and coagulate to lower the surface energy. For the synthesis of semiconductor nanospheres, the microfluidic reactor should be chemically and thermally stable; thus, the droplets and carrier fluid could be stable, non-volatile, non-interacting, and immiscible from ambient to reaction temperatures. Hitherto, these microparticles are widely applicable in biological, pharmaceutical, medical (such as tumor treatment, drug controlled-release, and multi drug loading), optical, electrical applications, and researches. Moreover, polymer microspheres and inorganic microspheres are of great interest due to their potentials in adsorption separation as adsorbent in wastewater treatment, as shown in **Figure 2** and **Table 3** [29].

4. Sorption performance of different functional micro-sorbents for pollutants removal

Pollution management is now one of the most challenging issue facing modern societies. Due to the increasing population as well as industrialization of most countries, some pollutants are being discharged into aquatic environment without further treatment. This has a negative impact on the environment. The advancement of microfluidic technologies has allowed the synthesis of functional sorbents with greater sorption capacity. This is because the structure of the sorbent can be easily modified during emulsion. Thus, microsorbents with different functional groups can be synthesized to remove certain pollutants. Chitosan is a material that is widely used to make adsorbent for pollutant removal due to its affinity in removing heavy metals. In this subsection, the sorption performance of different functional microsorbents will be discussed as well as the kinetic model and adsorption isotherm.

4.1 Application and sorption performance of chitosan-based microsorbents

Chitosan is a natural polymer material that is found in abundance. It is made from the chitin of crustaceans and shrimps. Due to its affinity with heavy metals, it is a material with great potential for biosorbent synthesis. For instance, polyethylenimine-chitosan microspheres are used to remove methyl orange and Congo red dyes. Based on empirical observations, the uptake of methyl orange dye ranges around 88–97%, whereas the uptake of Congo red dye ranges around 86–96% [55]. Zhai et al. [57] and Dong et al. [2] both have reported that the sorption performance of chitosan microspheres in the uptake of the common textile azo dyes. Apart from synthetic dyes, chitosan microspheres were also synthesized to remove copper (II) ions, the sorption performance was observed to be roughly 38.52 mg/g [29]. With the addition of polyacrylic acid, the sorption performance increased significantly [56]. Besides, Lv et al. [64] studied the sorption uptake of copper (II) ion with using polyethylenimine-poly(glycidylmethacrylate)-chitosan microsphere. Microfluidic synthesized ion-imprinted chitosan microspheres and thiourea-modified chitosan were also used to remove copper (II) ions. These studies have proved that microfluidic synthesized chitosan is a promising biosorbent for water remediation. Moreover, its mechanical intensity, sorption performance, and equilibrium adsorption amount of emerging contaminants are highly enhanced as compared to those conventional methods.

4.2 Application and sorption performance of non-chitosan-based microsorbents

Aside from chitosan, other microfluidic synthesized materials such as graphene oxide, silicon-based organic polymer, carbon, and silica were also used to be studied for wastewater treatment [11, 61–63, 65]. Copic et al. [61] reported that sodium dodecyl sulfate (SDS) and Congo red dye can be removed using carbon nanotubes microspheres. Li et al. [62] investigated that the synthesized hollow silica microspheres offer a much higher storage capacity as compared to conventional hollow nanospheres. Moreover, the drug detoxification capability of the hollow silica microspheres containing ethyl butyrate was tested on iodine removal [62]. The sorption capacity of iodine by silica microspheres goes up to 95% removal uptake. Lian et al. [63] studied the removal of toluene using polydimethylsiloxane microspheres synthesized via needle-based microfluidic devices. Ren et al. [65] synthesized anisotropic Janus microparticles loaded with Fe_3O_4 and MnO_2 nanoparticles for the adsorption of basic dyes in wastewater. The sorption performance of the dye uptake using Janus micromotors can be varied from 47 to 94%. Thus, the current adsorption isotherm, kinetic modeling studies, and sorption performance of each microfluidics generated micro-sorbents for different water applications have been listed in **Table 4**.

Microsorbents	**Application**	**Sorption performance**	**Adsorption isotherm**	**Kinetic modeling**	**Ref.**
Chitosan/polyethylenimine-chitosan microspheres	Adsorption of methyl orange (MO) and Congo red (CR)	MO uptake: 88–97% CR uptake: 86–96%	Not available	Pseudo-second-order	[55]
Polyethylenimine-poly(glycidyl methacrylate)-chitosan microspheres	Adsorption of copper (II) ions	q_{max}: 229 mg/g	Langmuir	Pseudo-second-order	[64]
Chitosan/chitosan-poly(acrylic acid) composite microspheres	Adsorption of copper (II) ions	Chitosan: q_{max}: 50 mg/g chitosan-poly(acrylic acid): q_{max}: 66–72 mg/g	Langmuir	Pseudo-second-order	[56]
Chitosan microspheres	Adsorption of copper (II) ions	q_{max}: 38.52 mg/g	Langmuir	Pseudo-second-order	[29]
Chitosan microsphere	Adsorption of methyl orange	q_{max}: 207 mg/g	Langmuir	Pseudo-second-order	[57]
Chitosan microparticles	Adsorption of methyl orange	MO uptake: 15% to >95% (dosage from 1 to 7 mg). q_{max}: 182 mg/g (40 ppm)	Langmuir	Pseudo-second-order	[2]
Thiourea-modified chitosan	Adsorption of heavy metal copper (II) ions	q_{max}: 60.6 mg/g (100 ppm)	Not available	Pseudo-second-order	[58]
Ion-imprinted chitosan microspheres	Adsorption of heavy metal copper (II) ions	q_{max}: 81.97 mg/g (Ce < 400 ppm)	Langmuir	Pseudo-second-order	[59]
Chitosan/silica hybrid microspheres	Adsorption of heavy metal copper (II) ions	q_{max}: 53 mg/g (100 ppm)	Not available	Not available	[60]
Graphene oxide/$MgCl_2$-graphene oxide microspheres	Adsorption of perfluorooctane sulfonate (PFOS)	PFOS uptake: >95–98% (in 2 min) q_{max}: 5300 mg/g	Not available	Not available	[11]
Carbon nanotube microspheres	Adsorption of sodium dodecyl sulfate (SDS) and congo red (CR)	Filtration efficiency: CR (84.7%), SDS (61.6%)	Not available	Not available	[61]

Microsorbents	Application	Sorption performance	Adsorption isotherm	Kinetic modeling	Ref.
Hollow silica microspheres with ethyl butyrate	Waste removal and drug detoxification/ iodine removal	Iodine uptake: 95% (in 30 seconds)	Not available	Not available	[62]
Poly(dimethylsiloxane) microspheres	Adsorption of toluene	Toluene uptake: 30–45% (350 ppm)	Not available	Not available	[63]
Poly-(ETPTA) /Fe_3O_4/MnO_2 bubble-propelled micromotors	Adsorption of methylene blue (MB)	MB uptake: 47–94% (6.67 ppm in 6.7% w/w H_2O_2)	Not available	Not available	[65]

Table 4.
Adsorption isotherm and kinetic modeling studies of microfluidics generated micro-sorbents on the uptake of each emerging contaminants.

5. Conclusion

Certainly, microfluidic technologies are a relatively new research with great potential for development to enable more cost-effective synthesis of functional sorbents. Currently, the state-of-the-art microfluidic reactors for water remediation and resource recovery are being implemented in small-scale applications. Example of microfluidic reactors includes microfluidic atmospheric pressure plasma reactor, which is used to degrade methylene blue dyes. Furthermore, the advances in microfluidic technologies have improved the production of micro sorbents using microfluidic technology. Many efforts are also pouring into researching different functional sorbents for removal of different pollutants in wastewater. The results of such research have culminated in the discovery the adsorption capacity and isotherm model of different micro sorbents, which gives insight on the suitable sorbents required for different pollutants.

At present, the need of highly effective water remediation and resource recovery has brought about mounting interest in the research of microfluidic technologies. Many breakthroughs had been achieved in such research which enabled highly specific and controlled synthesis of functional sorbents using microfluidic systems. However, there are still many barriers that prevent the implementation of microfluidic technologies on an industrial scale. The greatest challenge against microfluidic technologies is the economical aspect. Due to the highly specific characteristics of sorbents used in wastewater treatment, most microfluidic systems are highly specific as well. Sorbents used in different applications would require different microfluidic systems to synthesize. Thus, more research will need to be done in order for such problems to be overcome. Of course, environmental problem such as water remediation and resource recovery cannot be solved by microfluidic technology alone and will need other technologies to complement it.

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Conflict of interest

The authors declare that they have no conflicts of interest.

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