Fabricating MOF/Polymer Composites via Freeze Casting for Water Remediation

Coral Rogers 1, Daniel Pun 1, Qingshan Fu 2 and Haifei Zhang 1,*

1 Department of Chemistry, University of Liverpool, Oxford Street, Liverpool L69 7ZD, UK; sgcroger@liverpool.ac.uk (C.R.); sgdpun@liverpool.ac.uk (D.P.)
2 College of Material Science and Engineering, Sichuan University of Science and Engineering, Zigong 643000, China; sendysan@suse.edu.cn
* Correspondence: zhanghf@liverpool.ac.uk; Tel.: +44-151-7943545

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Abstract: Various porous materials have been used as adsorbents for water remediation. Among them, metal-organic framework (MOF) particles have been explored intensively, due to their size-controlled micropores and high surface areas. MOF nanoparticles are often used because of high external surface area and easy access to the micropores. However, recovering MOF nanoparticles, usually by filtration or centrifugation, is time-consuming and is difficult to scale up. We report here the preparation of porous MOF/polymer monoliths by freeze casting for water remediation. Chitosan and UiO-66 (Universitetet i Oslo) nanoparticles (including different surface functional groups) are used to prepare such monoliths. In order to improve the mechanical stability and the tendency of disintegrating in water, the freeze-dried UiO-66/chitosan monoliths are further treated by heating, washing with aqueous NaOH solution, or chemical crosslinking with glutaraldehyde. All these treated monoliths are used for adsorption of a herbicide methylchlorophenoxypropionic acid (MCPP) from aqueous solution. Particularly, the crosslinked chitosan/UiO-66 monolith achieves an adsorption capacity of 47.67 mg g⁻¹, with a 60 ppm MCPP solution. It is superior to that presented by the sole UiO-66 nanoparticles, exhibiting over a 30% increase in the adsorption capacity. The monoliths can be easily removed using tweezers, providing facile recyclability, which is advantageous for upscaling. The recycled monolith upheld approximately 75% of the adsorption capacity compared to the original monolith after three reuse cycles.

Keywords: monolith; chitosan; freeze casting; metal-organic framework; UiO-66

1. Introduction

Access to clean, safe water is critical for all living things. With the increasing population and ongoing industrialization, there is a great concern on the continuous deterioration of water quality. As a result, the ability to remove contaminants from water is becoming a major global concern [1]. Much research is carried out investigating the water remediation of different contaminants, such as heavy metal ions, radioactive materials, organic chemicals, and biological objects [1,2]. These contaminants come from natural and mainly human activities, such as mining, textile industry, pharmaceutical and agricultural waste, oil spillages, and many more [3]. Methods of water remediation investigated include photocatalytic degradation, oxidation processes, and the use of membranes and adsorbents such as activated carbon and various materials [1,4–7]. One of the widely investigated techniques is adsorption, due to its versatile process and moderate processing conditions required. Over the last few decades, the research in this area has included the use of activated carbon, porous materials, metal oxide nanoparticles, and biomass wastes as absorbents [1–7].
One type of material that has shown great potential in water treatment is metal-organic frameworks (MOFs) [8]. MOFs are hybrid organic-inorganic solids made up of metal nodes connected with organic linkers [8,9]. They have crystalline, highly porous structures with extremely large internal surface areas and regular porosity. MOFs can be easily tuned to have a desired functionality by careful selection of the metal ion and the ligand. The precise tunability of MOFs makes them applicable to a variety of processes, such as gas storage, catalysis, and separation processes [8]. The adsorption selectivity can systematically be altered by control of the pore size, morphology, and surface functionality of the MOFs [8,9].

For water remediation, the selected MOFs must be stable in water, ideally in a wide range of pH, temperature, and ionic strength values. However, the majority of MOFs are unstable in water, particularly at high/low pH and high temperature [10]. One of the water-stable MOFs is UiO-66, a zirconium-based MOF made up of twelve Zr6 clusters, connected via terephthalate linkers [11]. As such, UiO-66 has been used for water remediation [12,13], including the adsorption of methylchlorophenoxypropionic acid (MCP), a phenoxy acid commonly used in agriculture as an herbicide [14,15].

The use of MOF nanoparticles for applications involving liquid phase enhances mass transport due to high external surface area [9,15]. However, the disadvantages of using this procedure include tedious collection & recycling of MOF nanoparticles and the difficulty in upscaling. To address this issue, MOF monoliths [16,17], and more commonly MOF/polymer composites have been fabricated and used [14]. Among various methods of making nanoparticles/polymer composites [18,19], freeze-casting is a highly versatile and efficient process to make a wide range of porous materials, including polymer, ceramics, and composites [20,21]. The resulting materials exhibit highly interconnected ice-templating macropores and contain porosity/properties contributed by nanoparticles and polymers in the materials [14,17,20]. To prepare nanocomposites by freeze-casting, nanoparticles (e.g., ceramic nanoparticles, MOF nanoparticles, and/or organic nanoparticles) can be readily dispersed in a polymer solution, which is then frozen and freeze-dried to form the desired materials. Here, we report the preparation of MOF(UiO-66)/polymer monoliths by the freeze-casting approach and the use of such materials for water remediation (adsorption of MCP). UiO-66 nanoparticles with different functional groups and chemical crosslinking of the polymer are employed to improve the mechanical stability, recycling potential, and the adsorption performance of the composite monoliths. The easy recycling of MOF/polymer monoliths with high performance is demonstrated.

2. Materials and Methods

2.1. Reagents and Materials

Methylchlorophenoxypropionic acid (MCP), chitosan (medium and high molecular weight), zirconium chloride (ZrCl4), benzoic acid, terephthalic acid (BDC), 2-nitroterephthalic acid, 2-aminoterephthalic acid, N,N-dimethylformamide (DMF), and glutaraldehyde (GA, 25% water solution) were purchased from Sigma-Aldrich and used without additional purification. Hydrochloric acid (37%), deionized water, and standard GPR grade solvents were used routinely as required.

2.2. Preparation of UiO-66, UiO-66-NH2 and UiO-NO2 Nanoparticles

ZrCl4 (2 mmol), BDC (2 mmol), benzoic acid (20 mmol) were dissolved in HCl (37%, 0.66 mL) in 36 mL of DMF with stirring. The mixture was covered with aluminium foil and heated in an oven at 120 °C for 48 h. After cooling to room temperature, a white powder of UiO-66 nanoparticles was collected by centrifugation and washed with DMF at room temperature. The collected nanoparticles were dried overnight in a 60° oven.

The same procedure was followed for the preparation of the functionalised nanoparticles, UiO-66-NH2 and UiO-66-NO2, based on a previous report [22]. The BDC organic linker was replaced
with the functionalised analogue, 2-amino terephthalic acid, and 2-nitro terephthalic acid, yielding light yellow and white nanoparticles respectively.

2.3. Fabrication of Chitosan/UiO-66 Composites via Freeze Casting

Chitosan was used as the polymer to prepare the composite monoliths. An amount of 0.2 g of medium MW chitosan powder was dissolved with stirring, in 20 mL of deionized water with 120 µL of acetic acid. An amount of 0.2 g or 0.4 g of UiO-66 nanoparticles was then added into the 1 wt % chitosan solution, with rigorous stirring. The beaker containing the solution was slowly immersed into a bath of liquid nitrogen and kept in the bath for approximately 5 min. The frozen samples were freeze-dried for 48 h in a VirTis Advantage freeze-dryer to form dry chitosan/UiO-66 monoliths. The two monoliths with different chitosan-to-UiO-66 ratios were denoted as CM/UiO-66-1 (weight ratio of chitosan to UiO-66 was 1:1) and CM/UiO-66-2 (weight ratio of chitosan to UiO-66 was 1:2).

The same procedure was followed for UiO-66-NH$_2$ and UiO-66-NO$_2$ nanoparticles. High MW chitosan was also used to replace medium MW chitosan, but an extra 10mL of deionised water with 60 µL of acetic acid was added to the chitosan solution to aid with the dissolving. Similarly, the composites were denoted as the following CH/UiO-66-1 (weight ratio of high MW chitosan to UiO-66 was 1:1). Table S1 lists the chitosan/UiO-66 samples prepared and their descriptions, with post-treated samples also included.

2.4. Post-Treatment of Freeze-Dried Chitosan/UiO-66 Monoliths

The post-treatment was necessary to increase the mechanical stability of the composite monoliths in aqueous medium. The freeze-dried composite monoliths were disintegrated into small pieces in aqueous solutions during initial testing, which would remove the advantage of monoliths for easy recycling. The post-treatment methods included heating treatment (heated in a vacuum oven at 90 °C for 24 h), treatment with basic solutions, and chemical crosslinking as described below.

2.4.1. Base Treatment

The base treatment followed the same procedure as reported previously [14]. Briefly, the composites were immersed in 1M NaOH solution for 15 min. The NaOH-treated monoliths were then washed with deionized water until the pH value approached 7. Afterwards the washed monoliths were soaked in acetone for 30 min, replenished with fresh acetone 3 times, and then soaked in acetone overnight. Finally, the monoliths were soaked in cyclohexane for 1 h before air-drying in fume hood. Samples denoted as CM/UiO-66-NH$_2$-1 (BT), with BT standing for base treated.

2.4.2. Chemical Crosslinking of Chitosan with Glutaraldehyde

The procedure was slightly modified from a previous report [23]. Briefly, the freeze-dried chitosan/UiO-66 monoliths were rehydrated and further treated with 0.25% (w/v) glutaraldehyde (GA) solution at 50 °C for 4 h. The white monolith changed to a dark yellow colour. Subsequently, the monoliths were rinsed with deionised water six times to remove the excess GA and then freeze dried. The samples were denoted with GA (standing for glutaraldehyde crosslinking).

2.5. Water Treatment with MCPP Adsorption

Both UiO-66 nanoparticles and porous monoliths were employed for the adsorption of MCPP from its aqueous solution. Amounts of 10 mg for each of the test materials were added to 10 mL of MCPP solution with a concentration of 60 ppm, with gentle stirring. At scheduled intervals an aliquot of the MCPP solution was taken. For the adsorption testing of UiO-66 nanoparticles, 1.0 mL of MCPP solution was collected and centrifuged at 14,000 rpm. Then 150 µL of the supernatant phase was subject to the UV-vis analysis. For the assessment of monolithic composites, 150 µL of solution was taken directly for the UV-vis absorbance test. After the UV-vis analysis, the 150 µL solution was
replaced back to the 10 mL MCPP test solution. The concentration of the MCPP solution was evaluated by the UV absorbance at 279 nm with a UV spectrophotometer (MQX200, BioTek Instruments, Inc., Winooski, VT, USA). The concentration and the amount of MCPP were calculated according to the calibration curve obtained in this study (Figure S1). The MCPP amounts adsorbed by samples at different periods were calculated according to the following equation:

\[ q_t = \left( \frac{C_0 - C_t}{m} \right) V \] (1)

where \( C_0 \) is the initial concentration (ppm) and \( C_t \) is the concentration at time \( t \), \( m \) (g) is the mass of adsorbent, \( V \) (L) is the volume of the MCPP solution, and \( q_t \) (mg g\(^{-1}\)) is the MCPP amount adsorbed by the adsorbent at time \( t \).

2.6. Material Characterization

Sample morphology was determined using scanning electron microscopy (SEM, Hitachi S-4800, Hitachi Europe Ltd., Berkshire, UK). Before imaging, all samples were sputter-coated with a thin gold layer (~2 nm) using an automated sputter coater (Emitech K550X, Quorum Technologies Ltd., Laughton, UK). Powder X-ray diffraction (PXRD) patterns were collected on a Bruker-AXS D8 advanced diffractometer with CuK\(\alpha\) radiation source. Fourier transform infrared (FTIR) spectra were collected using a Perkin-Elmer 457 spectrometer (PerkinElmer, Buckinghamshire, UK).

3. Results and Discussion

Chitosan is only soluble in acidic water. When preparing chitosan/UiO-66 composites, UiO-66 nanoparticles have to be dispersed in aqueous chitosan solution under acidic condition. Thus, the use of water-stable MOFs is highly important for the fabrication of chitosan composites. It has been reported that functionalized UiO-66, namely UiO-66-NH\(_2\) and UiO-66-NO\(_2\), prepared from the BDC organic linkers with a nitro- or amino-group attached, have shown improved water stability under harsh pH conditions compared to the parent UiO-66 [10,22]. UiO-66-NO\(_2\) showed particularly high chemical stability in basic condition, with the retention of the crystalline structure after being soaked in NaOH solution [22]. Therefore, chitosan composites with both UiO-66 nanoparticles and functionalized UiO-66 nanoparticles are prepared and evaluated. Figure S2 shows the FTIR spectra of UiO-66, UiO-66-NH\(_2\) and UiO-66-NO\(_2\) nanoparticles in this work. The peaks observed at 1578 and 1394 cm\(^{-1}\) are characteristic of the in- and out-of-phase stretching modes from the carboxylate group associated with the organic linker. For UiO-66-NH\(_2\), the amino group can be distinguished at 3504 cm\(^{-1}\) and 3381 cm\(^{-1}\), which can be attributed to asymmetric and symmetric N-H stretches respectively. For UiO-66-NO\(_2\), the asymmetric NO\(_2\) stretching vibration can be assigned to the peak at 1536 cm\(^{-1}\).

3.1. Freeze-Dried and Post-Treated Chitosan/UiO-66 Composites

Porous composites are obtained after freeze-drying the frozen suspension of UiO-66 nanoparticles in aqueous chitosan solution. As characterized by scanning electronic microscopy (SEM), all the monoliths (with UiO-66, UiO-66-NH\(_2\), and UiO-66-NO\(_2\) nanoparticles) show ice-templated structures and the presence of MOF nanoparticles. Figure 1 shows the SEM images of the composites (CM/UiO-66-NO\(_2\)) made from medium MW chitosan and UiO-66-NO\(_2\) nanoparticles after freeze drying. Similar pore morphologies and MOF nanoparticles were observed for CM/UiO-66 composites and CM-UiO-66-NH\(_2\) composites (Figures S3 and S4).
They can therefore often be overlapped with these common functional groups, which are apparent within both chitosan and the MOF nanoparticles. Carbonyl and alkene double bonding regions [25] are often very hard to distinguish as they exhibit adsorptions close to the carbonyl and alkene double bonding region [25]. They can therefore often be overlapped with these common functional groups, which are apparent.

This is because of the better performance of UiO-66 nanoparticles and composites for the adsorption of MCPP, discussed below. UiO-66 nanoparticles were synthesised with established procedures [11,22]. The freeze-drying of UiO-66-NO$_2$ was retained in the composites although the heat treatment reduced the crystallinity of UiO-66 nanoparticles in aqueous polymer solution was known to retain the crystallinity of UiO-66 [14]. Figure S6 confirms the crystallinity of UiO-66-NO$_2$ was retained in the composites although the heat treatment reduced the crystallinity.

Overlapping peaks are observable, unlike the smooth peaks seen in spectrum of the un-crosslinked monolith. Double-bonded nitrogen groups are often very hard to distinguish as they exhibit adsorptions close to the carbonyl and alkene double bonding region [25]. They can therefore often be overlapped with these common functional groups, which are apparent.

The sizes of UiO-66-NO$_2$ nanoparticles are in the approximate range of 50–100 nm (Figure 1A). The sizes of UiO-66-NO$_2$ nanoparticles are in the approximate range of 50–100 nm (Figure 1A). Figure 1B clearly shows the nanoparticles embedded in and on the surface of the layered porous chitosan structure; the ridges can be clearly seen (Figure 1C), which are characteristic of the ice-templated materials [20,21]. In between the ridges the surface of the chitosan appears to be fairly smooth. After heating treatment, the nanoparticles can still be seen embedded in the material and seem to be of similar sizes (Figure 1D,E). The surface appears to be rougher than the untreated samples, showing a flaked appearance. Similar results can be seen for the NaOH treated sample, as shown in Figure 1F,G. The surface appears significantly rougher subsequent to the base treatment, potentially removing some of the nanoparticles from the surface layers. Similar observations were noted for the composites with UiO-66 and UiO-66-NH$_2$ nanoparticles.

Only the chitosan/UiO-66 composites were treated by chemical crosslinking with glutaraldehyde. This is because of the better performance of UiO-66 nanoparticles and composites for the adsorption of MCPP, discussed below. UiO-66 nanoparticles can be observed (Figure 1H) and the macroporous structure remains after crosslinking (Figure 1I). The crosslinking of chitosan with glutaraldehyde can be confirmed by FTIR analysis with a new peak from the C=N bond, resulted from the reaction between the amine group on chitosan and the aldehyde group [24]. The FTIR spectra of the composite monoliths before and after the crosslinking are very similar (Figure S5). However, on closer inspection of the peaks in region 1550–1700 cm$^{-1}$, overlapping peaks are observable, unlike the smooth peaks seen in spectrum of the un-crosslinked monolith. Double-bonded nitrogen groups are often very hard to distinguish as they exhibit adsorptions close to the carbonyl and alkene double bonding region [25]. They can therefore often be overlapped with these common functional groups, which are apparent.

Figure 1. Pore structure by SEM imaging of (A) UiO-66-NO$_2$ nanoparticles, (B,C) CM/UiO-66-NO$_2$ (1:1) freeze dried composite, (D,E) CM/UiO-66-NO$_2$ composite after heat treatment (1:1), (F,G) CM/UiO-66-NO$_2$ (1:1) composite after base treatment, and (H,I) glutaraldehyde-crosslinked CM/UiO-66 (1:1).
within both chitosan and the MOF nanoparticles. Another problem is that only a small degree of crosslinking was achieved. According to Pratt et al. [26], the intensity of the imine signature increases with amount of the glutaraldehyde content. Therefore the analysis of the spectra is difficult as the peak intensity will be relatively low. In spite of these difficulties, the crosslinking of chitosan can be confirmed by the improved stability in water treatment, as demonstrated in the section below.

UiO-66 nanoparticles were synthesised with established procedures [11,22]. The freeze-drying of UiO-66 nanoparticles in aqueous polymer solution was known to retain the crystallinity of UiO-66, as confirmed by powder x-ray diffraction (PXRD) analysis [14]. Figure S6 confirms the crystallinity of UiO-66-NO$_2$ was retained in the composites although the heat treatment reduced the crystallinity while the composites treated with NaOH solution showed an amorphous material. Poor crystallinity was observed for the chitosan/UiO-66-NH$_2$ composites (Figure S7). Like other MOFs, UiO-66 nanoparticles show high surface areas and the functionalized UiO-66 nanoparticles exhibit lower surface areas due to the presence of functional groups (-NH$_2$ or -NO$_2$) in the framework [11,22]. Commonly, MOF materials show a range of surface areas, depending on preparation methods, crystallinity, and post-treatment procedure. The UiO-66 nanoparticles synthesized in this study showed a surface area of 1034 m$^2$ g$^{-1}$ and the CM/UiO-66 (1:2) gave a surface area of 339 m$^2$ g$^{-1}$. For water treatment or other liquid phase application, the porosity and macropores can be measured by Hg intrusion porosimetry [14].

3.2. Adsorption of MCPP from Aqueous Solutions

UiO-66 nanoparticles with different functionalities were first examined with 60 ppm MCPP solution. As shown in Figure 2, the functionalized UiO-66 nanoparticles (UiO-66-NH$_2$ and UiO-66-NO$_2$) yield lower adsorption capacity, particularly with UiO-66-NO$_2$ nanoparticles being about five times lower. This can be attributed to the lower surface area and hindered access to the micropores due to the presence of the functional groups.

![Figure 2. Profiles of the adsorbed quantity of methylchlorophenoxypropionic acid (MCPP) versus soaking time by dispersing (10 mg) of nanoparticles in 10 mL of aqueous solution of MCPP (60 ppm). Each of the tests in this study were carried out three times.](image)

The freeze-dried chitosan/UiO-66 composite monoliths were disintegrated in water, forming cloudy suspensions. However, after heating treatment, the monoliths were largely stable after soaking in 60 ppm MCPP solution for three h, particularly for the chitosan/UiO-66-NO$_2$ monolith where the MCPP solution was still clear despite the presence of some small pieces (Figure S8). The adsorption of the heat-treated (HT) composite monoliths with 60 ppm MCPP solution (Figure 3) shows the
improved adsorption capacity for UiO-66-NH$_2$ and UiO-66-NO$_2$ compared to their nanoparticle powders. This is because of the relatively high adsorption capacity of chitosan for MCPP and the interconnected macroporosity of the monoliths [14]. An obvious sigmoidal shape of the adsorption curve is shown for the sample CM/UiO-66-1 (HT). It is less obvious for the other two samples. Generally, this phenomenon may be attributed to the dense skin of the adsorbents after heat treatment. The dense surface or smaller pores impede the uptake of the solution and transport of the MCPP, resulting in low adsorption initially. With time, the adsorbent becomes more hydrated, leading to a more swollen scaffold, facilitating mass transport and higher adsorption. However, the performance of the composite monoliths with functionalized UiO-66 nanoparticles is still lower than that of the standard (un-modified) UiO-66 nanoparticles.

![Graph showing adsorption profile](image)

**Figure 3.** Profiles of the adsorbed quantity of MCPP versus soaking time by immersing the composites (10 mg) in 10 mL of aqueous solution of MCPP (60 ppm).

The composite materials prepared with the amino and nitro functionalised MOF nanoparticles were subject to treatment with aqueous NaOH solution, followed by further washes with acetone and cyclohexane. The aim of the base treatment was to remove the residual acid present from the composite fabrication procedure and render the monoliths more stable in aqueous solution. Acetone and cyclohexane were used for a solvent exchange process to reduce shrinkage on drying. It was noticed that the base-treated samples were very stable in water, consistent with our previous findings [14] (Figure S9). These functionalised MOFs were shown to be more stable compared to the parent analogue, within acidic and basic conditions [10,22]. However, the PXRD analysis on these samples showed that the MOF crystalline structures had been destroyed by the base treatment.

Surprisingly, the adsorption tests with MCPP solution and the monoliths showed unusual results. The concentration of MCPP in the solution was calculated from the UV absorbance at 275 nm, characteristic of MCPP. A decrease in peak intensity at 275 nm over time would be expected for the adsorption of MCPP by the chitosan/MOF monolith. However, for the base-treated chitosan/UiO-66-NO$_2$, an increase in the intensity of the absorbance peak at 275 nm was observed, along with an increased peak appearing at around 230 nm and a shoulder forming around 300 nm (Figure S9). This was believed to be due to the composite leaking materials that present with UV absorbance in the same region as MCPP peak. To prove this, the composite material was immersed in pure deionised water. After a period of time, the solution was subject to UV-Vis analysis, which showed the appearance of absorbance peaks corresponding to those appearing within MCPP solution (Figure S10). This confirms the material leaking from the base treated monolith. A similar observation was noted for the amino functionalised monolith after base treatment but there was no such problem...
for the chitosan/UiO-66 composites after the base treatment (Figure S11). Further investigation is required to identify the leaked materials but it indicates that the base treatment is not suitable for chitosan/UiO-66-NO$_2$ and chitosan/UiO-66-NH$_2$ monoliths.

Due to the relative low performance of UiO-66-NO$_2$ and UiO-66-NH$_2$ nanoparticles & monoliths, the study on chemical crosslinking of the composite monoliths with glutaraldehyde was focused on chitosan/UiO-66. This procedure was found to be highly effective at stabilising the monolith within MCPP solution. The monolith could be easily picked out of solution using tweezers after the six-hour adsorption testing period (Figure S12). This offers the potential of facile recyclability which is advantageous for industrial purpose.

The adsorption profile of the glutaraldehyde-crosslinked absorbent is compared with that of the nanoparticles and the base-treated samples, as shown in Figure 4. The crosslinked absorbent shows a superior adsorption profile than both UiO-66 nanoparticles and the base-treated composite monolith, approximately 30% increase in the absorption capacity compared to the sole UiO-66 nanoparticles. The better performance of the crosslinked composites can be attributed to: (1) The interconnected ice-templated porous scaffold provides enhanced mass transport; (2) Chitosan itself is also a very good adsorbent for MCPP [14]. This crosslinked monolith material therefore presents as a promising material for the absorption of MCPP.

![Figure 4](https://example.com/figure4.png)

**Figure 4.** Absorption profiles of the absorbent materials including UiO-66 nanoparticles, base-treated (BT) medium weight chitosan/UiO-66 (polymer: MOF = 1:1 in mass), and glutaraldehyde (GA)-crosslinked medium weight chitosan/UiO-66 (polymer: MOF = 1:1 in mass) against the soaking time within 60 ppm MCPP solution.

Adsorption kinetics and isotherm studies and adsorption mechanism for the adsorption of MCPP on chitosan/UiO-66 composites were reported before [14]. This study is focused on how to improve the stability of the chitosan/UiO-66 composites while maintaining their performance. As such, the recovery and reusability of an adsorbent is highly important. The ideal adsorbent needs to have facile recovery and a repetitively high adsorption capacity after reuse cycles. UiO-66 nanoparticles have previously displayed good performance for the adsorption of MCPP from water. The retrieval for reuse was shown to be restricted by the tedious centrifugation process required [15]. This time-consuming process raises the cost of water remediation, limiting the potential for process upscaling. Therefore, the use of a stable chitosan/MOF monolith was investigated to tackle this problem, where the monolith could be easily picked up instead of using the energy- and time-consuming centrifugation (or filtration) process. The glutaraldehyde-crosslinked monolith has shown to give a superior adsorption capacity to
the nanoparticles, while maintaining mechanical stability. The monolith could be simply picked out of the solution using tweezers, offering the potentials for facile recovery.

The performance of the crosslinked adsorbent was further examined to assess its reuse viability. The monolith was immersed within the MCPP solution for 6 h with stirring. An aliquot of the final solution was taken and subject to UV-vis analysis. Recovery of the monolith was facile, simply being picked out of solution using tweezers. Removal of MCPP from the adsorbent was carried out by soaking in deionized water, followed by three replenishes with ethanol. Finally, the adsorbent was dried under vacuum, and the adsorption process repeated to test the recyclability. The adsorption capacity obtained from three reuse cycles are shown in Figure 5. After three cycles, the monolith still exhibited a high adsorption capacity, 35.67 mg g\(^{-1}\), within 10 mL of 60 ppm MCPP aqueous solution. Still presenting a higher capacity than that of the sole UiO-66 nanoparticles. The performance of the recycled monolith reached approximately 75% of adsorption capacity compared to the adsorbed amount by the fresh adsorbent. These results demonstrate the glutaraldehyde-crosslinked chitosan/MOF monoliths as a very promising adsorbent for MCPP.

![Figure 5. Reusability of glutaraldehyde-crosslinked CM/UiO-66 (polymer: MOF = 1:1) for the adsorptive removal of MCPP from 10 mL of 60 ppm MCPP aqueous solution.](image)

### 4. Conclusions

In conclusion, porous polymer/MOF composites, specifically chitosan/UiO-66, are fabricated using a freeze-casting approach. The resulting materials show the presence of UiO-66 nanoparticles and ice-templated macropores. UiO-66 nanoparticles functionalized with –NH\(_2\) or –NO\(_2\) groups are also used and investigated due to their expected stability in water under different pH conditions. As expected, the freeze-dried composites are not stable in water and could disintegrate readily. In order to be used for water remediation as monoliths, the freeze-dried composites are further treated by heating treatment, base solution (NaOH) treatment, and chemical crosslinking of the polymer matrix using glutaraldehyde. After the treatments, the monoliths are stable in water and can be easily picked up using tweezers, thus avoiding the use of time-consuming centrifugation for recycling MOF nanoparticles and the associated costs. More excitingly, when tested for the adsorption of MCPP, the chemical-crosslinked polymer/MOF monoliths showed better performance than the highly expected UiO-66 nanoparticles (about 30% increase in adsorption capacity), with facile recycling by easily picking up with tweezers. These crosslinked monoliths also demonstrate good recycling potential. After three reuse cycles, upholding 75% of the adsorption capacity is achieved, compared to the fresh absorbent. In principle, this method can be extended to fabricate highly interconnected porous composite monoliths, including the use of other polymers, other MOF nanoparticles, ceramic...
nanoparticles, and inorganic nanoparticles, tailored for target applications with the advantages of composites, monoliths, and the mass transport-enhanced macropores.

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**Author Contributions:** C.R. participated in experiment design, carried out the experiments, and completed the draft report; D.P. and Q.F. took part in experiment design and/or help with the freeze-casting process and dye adsorption study; H.Z. conceived & designed the experiments, analysed the data, and wrote/finalized the manuscript.

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