Selection of binder recipes for the formulation of MOFs into resistant pellets for molecular separations by fixed-bed adsorption

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Abstract

The formulation of metal-organic frameworks (MOFs) materials into resistant structures is a key step towards their use in adsorptive separation processes. In this study, ZIF-8 crystals have been formulated into resistant pellets with various binders by a simple extrusion-crushing-sieving (ECS) approach. 55 recipes were evaluated with a series of stability tests – mechanical stability upon friction, acid/base stability, hydrothermal stability and long-term stability for storage over several years – as well as with a set of adsorption and separation experiments. The stability tests have highlighted that PVF (polyvinylformal) is the most promising binder to generate resistant pellets with ZIF-8 crystals for the adsorptive recovery of n-butanol in the acetone-butanol-ethanol (ABE) fermentation process, while other binders, including methylcellulose, may find their use in gas/vapor adsorption processes. Adsorption of ethanol vapor has shown that the formulation results into a decrease of adsorption capacity, which is proportional to the binder fraction, while having no effect on the adsorption kinetics. On the other hand, packed bed experiments in liquid phase have indicated that ZIF-8 composite materials maintain the separation ability of the unformulated ZIF-8, but also that the binder results into an unfavorable additional mass transfer resistance. These results have been supported by complementary porosimetry measurements with Ar and Hg, indicating that the composite materials are very porous with narrow pore-size distributions. From this experimental work, various formulation recipes have been identified, which may lead to resistant MOF composite materials for adsorptive separations.

Keywords

Porous Materials, MOFs, ZIF-8, Shaping, Powder Processing, Adsorption
1. Introduction

Within the family of Metal-organic frameworks (MOFs), the Zeolitic Imidazolate Frameworks (ZIFs) have gained a lot of attention due to their stability together with a large chemical and structural tunability, offering new opportunities for adsorption applications [1,2]. Recently, we identified a promising ZIF for the recovery of renewable organic compounds from aqueous mixtures [3]. In particular, the ZIF-8 MOF material showed remarkable properties for the separation of bio-butanol from ABE (acetone-butanol-ethanol) fermentation broths, outperforming traditional materials [3,4]. Towards its application in an adsorptive separation process, ZIF-8 must be shaped into a resistant structure, which, moreover, (if possible) enhance mass and heat transfer, while maintaining the interesting properties of the unformulated material [5].

In practice, many adsorptive separation processes are operated using fixed beds packed with adsorbent particles through which mixtures are pumped and separated [5]. Unformulated porous materials, commonly being in the form of small crystals or powder, are generally not used in fixed beds due to the large pressure drop such fine particles generate [5]. For that reason, porous materials are shaped into larger particles, usually made of crystals or powder strongly agglomerated together by a binder, such as a polymer or clay [5-8]. Although MOF materials containing binders were made in a limited number of studies [9-16], no clear criteria are available to select a binder for a given application and which, moreover, results into resistant pellets. Furthermore, only very limited work on the formulation of MOFs is present in the literature and formulation recipes remain often unpublished and secret within companies.

Therefore, in this work, an extensive screening and evaluation of various binders and recipes to make ZIF-8 pellets is presented, specifically towards their use in the recovery of biobutanol from aqueous mixtures by fixed-bed adsorption. Starting from the selection of the binders, based on criteria related to the abovementioned application of the ZIF-8 MOF, pellets are made by a simple extrusion-crushing-sieving (ECS) approach. In order to identify suitable binder formulation procedures, pellets are evaluated with stability tests, including mechanical strength upon friction, storage over several years, or dissolution in acid/base environment, as well with various adsorption and separation experiments.
2. Material and Methods

2.1. Material

ZIF-8 powder was bought from Sigma-Aldrich. Various binders and solvents (see Supporting information, Table S1 for more details) were used to produce ZIF-8 composite particles (see below for more details). An overview of the different solvents and binders is provided in Figure 1, with the binder fraction, given in weight percent (wt%), relative to the total solid mass (i.e. binder and ZIF-8 powder). Adsorption isotherm measurements and fixed-bed separation experiments were carried out with ethanol (99.7%, VWR Chemicals), n-butanol (99.5%, Sigma-Aldrich), acetone (99.98%, Fisher Sci. UK) and Millipore water (SIMPAOD2-filter). Argon (>99.9999 %, Air Liquide) and mercury (impurity <10 ppm) were used in porosity analyses (see below for more details). Aqueous solutions with varying pH were made with acetic acid (pure, Merck) and an ammonium hydroxide (in solution 28%, Fluka) diluted in Millipore water.

![Figure 1. Overview of binder fraction, binder type and solvent type used in the formulation of ZIF-8 pellets.](image)

2.2. Formulation

Binder-free pellets were produced by pressing the powder into a cake at 65 MPa. The cake was then broken into pellets and sieved at specific particle size ranges (see further). The effect of powder pressing on the adsorption properties of ZIF-8 was proven to be negligible, as discussed elsewhere [17]. ZIF-8 pellets with binder were produced by mixing 1g ZIF-8 crystals with a binder (Fig. 1) and gradually adding solvent until a thick slurry was...
obtained. The slurry was subsequently extrudated with a syringe (nozzle diameter of 2 mm) on an aluminum foil and dried overnight at open air. Afterwards, the extrudates were crushed and sieved at specific particle size ranges (Fig. 2). The binder fraction (relative to the total solid mass, which includes the binder and ZIF-8) was varied from 7.5 to 30 wt% (Fig. 1). The solvent was changed depending on the binder type (Fig. 1). 55 combinations of binders (i.e. type and fraction) and solvents with ZIF-8 powder were made and evaluated (see Table S2, Supporting Information). Methylcellulose and clay binders (i.e. bentonite and kaolin) were mixed with ZIF-8 powder and water. Following the extrusion and the first drying step (see above), the ZIF-8/clay pellets were also baked overnight at 823 K under nitrogen flow. For silica, slurries were prepared with water, iso-octane or tetrahydrofuran (THF). Binders cellulose-acetate (CA), polyetherimide (PEI), poly(1,4-phenylene-ether-ether-sulfon) (PFEES), polystyrene (PS), polyvinylchloride (PVC) and polyvinylformal (PVF) were first dissolve in 10 ml solvent, dimethylsulfoxide (DMSO), dimethylacetamide (DMA) or dimethylformamide (DMF), at 353 K for 40 minutes prior being mixed with the ZIF-8 powder. In case of DMSO use, the extrudates were additionally dried in an oven at 373 K after the first (open air) drying step. The binder content of pellets used in the breakthrough experiments (see further) was also verified by energy dispersive X-ray microscopy (EDX, see further for more detail).

![Figure 2. Optical and SEM (scanning electron microscope) images of ZIF-8 crystals (left upper), extrudates (left bottom) and pellets (right).](image-url)

### 2.3. Gravimetric method

Vapor phase adsorption isotherms of ethanol on ZIF-8 powder and pellets were measured with a gravimetric method. About 5-10 mg ZIF-8 material (i.e. powder, binder-free pellets or composite pellets) was placed into the balance sample holder and activated for two hours at 523 K under an inert environment (i.e. pure helium or nitrogen gas). After cooling down to 323 K, the adsorbent was contacted with an ethanol vapor enriched stream, which was obtained by bubbling an inert carrier gas through a container filled with liquid ethanol at 180 ml/min and a controlled temperature. The weight change of the adsorbent sample was monitored until equilibrium was
reached with the surrounding atmosphere. This was repeated for different ethanol partial pressures. The ethanol partial pressure was varied by changing the temperature of the liquid container and/or by dilution with a pure helium gas stream.

2.4. Stability tests

The mechanical, acid/base and hydrothermal stabilities of the ZIF-8 composite particles were evaluated by visual and manual inspections of the pellets (given in arbitrary units, a.u., see results). Scores have been attributed based on the observed attrition and collapse of the particles: ranging from 0 to 6 for very poor to excellent stability. The stability tests were performed by preliminary rudimental approaches to screen recipes in a simple and fast manner. The mechanical stability was assessed by exerting manually friction and pressure on the pellets on a flat surface. The acid/base stability was determined by assessing their dissolution in the liquid solutions of different pH, which was altered by changing the amount of ammonium hydroxide and acetic acid in the solution, chemicals typically found in fermentation processes [18-20]. The hydrothermal stability was assessed to evaluate the stability different materials under conditions used for desorption [3-4]. This was performed in the same way as the acid/base stability tests, but with samples being contacted with hot water (i.e. Millipore water) at 353 K for 4 hours. Finally, adsorption capacities were measured again after three years of storage at ambient conditions (circa. 80% relative humidity and 298 K) to determine the stability of the samples over time after shaping and contact with air.

2.5. Breakthrough experiments

Breakthrough experiments were performed with ZIF-8 pellets (250-450 microns particle size range) packed in columns (15 cm length and 0.45 cm inner diameter) through which aqueous mixtures containing acetone (1 wt%), n-butanol (2 wt%) and ethanol (0.5 wt%), diluted in water, were pumped at 0.5 ml/min and 298 K. The separation performances of composite materials (i.e. with binder) were compared to that of the ZIF-8 binder-free particles. Prior to being contacted with the liquid stream, the packed bed was placed under nitrogen flow of 30 mL/min at 423 K for an hour. Afterward, the system was equilibrated with pure Millipore water. Next, the aqueous solution was pumped through the column. Liquid samples were collected at the column outlet and analyzed by gas chromatography. Breakthrough curves were obtained by plotting the outlet concentration as a function of time. The amount n-butanol adsorbed \( q \) (g/g) was calculated from the mass balance over the column:

\[
q = \frac{(F \tau - \epsilon V)}{m_{ads}} c_o
\]

with \( F \), \( \tau \), \( \epsilon \), \( V \), \( m_{ads} \) and \( c_o \) denoting the volumetric feed flow rate (ml/min), the average breakthrough time (min), the total bed porosity, the column volume (ml), the adsorbent mass (g) and the n-butanol feed.
concentration (g/ml), respectively. The total bed porosity was determined as the sum of the interparticle voidage in the bed, assuming loose random packing, and the total intraparticle porosity obtained from mercury porosimetry (see Section 2.6). Assuming that the change in fluid velocity is negligible, the average breakthrough time was calculated from equation (2):

\[
\tau = \int_0^\infty \left(1 - \frac{c}{c_0}\right) dt
\]

(2)

with \(c\) and \(c_0\) representing the column outlet concentration and the feed concentration.

2.6. Ar and Hg porosimetry

Argon adsorption/desorption isotherms at 87 K were measured using an AUTOSORB-1 (Quantachrome) for ZIF-8 powder and pellets, which were activated at 423 K under vacuum for 3 hours. Mercury porosimetry measurements were performed with 2 Thermo-Finnigan porosimeters calibrated with ERM FD121 and FD122 standards. Before the measurements, samples were dried in an oven at 423 K under vacuum. After being transferred to the dilatometers, experiments were started at vacuum, followed by a stepwise increase in pressure up to 2000 bar. Calculations were performed with a contact angle of 140° and a surface tension of 480 Dyne/cm at 298 K. The data were analyzed with the traditional Mayer and Stowe method. The analysis at low pressure provides the particles size and pore size between the particles, while the high-pressure Hg intrusion data gives the pore size in the particles.

2.7. SEM – EDX analysis

Scanning electron microscopy (SEM) and electron dispersive X-rays (EDX) spectroscopy were used to characterize the structural and chemical bulk properties of the materials, respectively, using a JEOL JSM-IT300 device. The different samples were stabilized on the sample holder with carbon tape and analyzed under vacuum (circa 10^{-4} Pa) and at a voltage of 10 kV. The chemical bulk composition was calculated as the average of several crushed particles and the measurement on the surface of three different single particles with an observation plane of about 100 \(\mu m\) by 100 \(\mu m\). The amount of binder was estimated from the difference in zinc signal between the composite material and the pristine MOF. In addition, the ZIF-8 powder was visualized with a QUANTA FEG SEM device under vacuum (circa 10^{-5} Pa) and a voltage of 200 V.
3. Results and Discussion

3.1. Formulation

The formulation of porous materials relies a lot on trial-error. In order to reduce the number of chemicals to be tested, binders were selected based on criteria related to the application of ZIF-8 for the separation of n-butanol from aqueous mixtures [3-4]. Consequently, binders were chosen depending on their hydrophobicity, thermal stability for regeneration of the adsorbent (up to 353 K) [3-4] and ease of dissolution in the organic solvent used in the formulation recipes (see Fig. 1, *vide supra*, and Supporting Information Table S2). From this selection of formulation recipes, some binders did, however, show no compatibility or strong agglomeration with the ZIF-8 crystals, independently of the used solvent or binder fraction, with extrudates falling apart after the drying step and/or any further manipulation. This happened with silica or PFEES, and they were, therefore, excluded for further examination in this work. Furthermore, the clays, bentonite and kaolinite, which are typically used as binders for zeolites [5-8], also did not result in strong extrudates, unless they were baked. An attempt was made to bake the extrudates under inert conditions (i.e. pure nitrogen) to avoid degradation of the ZIF-8 material. Although this resulted in strong extrudates, degradation of the ZIF-8 material could not be avoided as seen from the difference in color between baked pure clay and ZIF-8 binder-free pellets (white), and the baked composite extrudate (black), as well as the dramatic change in adsorption capacities and isotherm shape (see Supporting Information Fig. S2). As a result, clay binders were also excluded for further examination in this study. On the other hand, the other binders (Fig. 1) led to strong extrudates, however, methylcellulose was also not considered further in this work because it completely dissolves back in presence of water, which is undesired for the specific application of n-butanol separation from aqueous mixtures [3-4]. Nevertheless, methylcellulose could be considered as a binder for studies on gas or vapor adsorption under dry conditions or at low humidity. Besides that, problems arose also with the polystyrene binder. Although ZIF-8/PS pellets could be produced, the dissolution of polystyrene in the solvent was slow. Consequently, separation experiments with this composite material were not performed (see Section 3.4), where large amounts of material are required to be packed into the columns. Second to last, most samples in this work were made with DMF as solvent (see further), because it dissolves the considered binders easily, but also because it is used in synthesis routes of the ZIF-8 MOF [21]. This gives the opportunity to combine the synthesis with the formulation of ZIF-8 crystals. Finally, in order to gain a microscopic view of the observed ZIF-8/binder’s (in)compatibility for the different tested formulation recipes, a systematic study could be conducted to evaluate the effect of binder and solvent properties, such as molecular weight, cross-linking and functional groups, on the interaction and agglomeration with ZIF-8 crystals, but is beyond the scope of current work. Such study appears even more interesting because the current knowledge presented in the literature (i.e. various techniques, different materials and limited information on the binder properties) does not allow a direct comparison with the results of our work.
3.2. Adsorption isotherms

From the remaining (selected) binders, the different composite materials were evaluated by measuring vapor phase adsorption isotherms of ethanol. Figure 3 (left) shows the adsorption isotherms of ethanol on the different composite materials. All materials display a decrease in capacity compared to the ZIF-8 powder, while binder-free pellets possess an identical adsorption isotherm (see elsewhere [17]). A decrease in saturation capacity (at 127.5 mbar) from 0.28 g/g to about 0.24 g/g is proportional to the amount of it (i.e. 15%) in the composite material. Deviations in binder content (see for example further Table 1) may occur from batch to batch due to the difficulty to control the amount of binder which agglomerates with the ZIF-8 crystals as well as the amount remaining after the crushing step. In addition, the isotherm shape is also maintained for pellets containing a binder. This suggests that the equilibrium adsorption properties of ZIF-8 are not affected by the presence of the binder. Such isotherm shape can be attributed to the adsorption of a polar adsorbate on an apolar adsorbent [22-26]. Furthermore, the ethanol uptake curves of ZIF-8 composite materials are almost identical to that of the powder. The adsorption kinetics of ethanol, under vapor phase conditions, into the ZIF-8 structure appear unaffected by the formulation of the ZIF-8 crystals in composite materials (Fig. 3, right). Other conditions, for example with a packed bed subjected to a fluid stream (see further), may reveal additional mass transfer resistances (i.e. diffusion through fluid film or heat effects). The results shown in Figure 3, prove that the original ZIF-8 properties are maintained with the selected binders and formulation methods.

![Figure 3](image)

**Figure 3.** Adsorption equilibrium (left) and kinetics (right, pressure step from 5 to 10 mbar) of EtOH vapor on ZIF-8 powder and composite pellets (with 15 wt% binder, DMF solvent) at 323.15: (○) ZIF-8 powder and composite materials with binders (□) CA, (■) PVC, (△) PVF, (●) PEI and (♦) PS. Comparison of ZIF-8 powder and binder-free pellets can be found elsewhere [17].

3.3. Stability tests

Afterwards, the mechanical stability of the composite materials upon friction was tested. It can be noticed from Figure 4 that, as expected, by increasing the binder fraction, the mechanical stability of the pellets is improved,
since the binder works as a glue or gel network holding the ZIF-8 crystals together. The results also indicate that the binder type and the solvent used in the formulation protocols may influence the stability of the ZIF-8 pellets, but differences are very small. Pellets with PVC and PVF binders (combined to the DMF solvent) appear to yield the best mechanical resistance. Other techniques, such as nano-indentation [27], micro-indentation [27] and dynamic mechanical analysis [28], were used to quantify the hardness or mechanical strength more accurately. Unfortunately, no reliable results could be obtained due to the material heterogeneity, surface roughness and required sample size. Solving these problems falls beyond the scope of this study.

**Figure 4.** Mechanical stability upon friction of ZIF-8 composite pellets for different amount of binders and solvents: a) 7.5 wt%, b) 15 wt% and c) 30 wt% binder.

The results of the acid/base stability assessments are shown in Figure 5 (left). On one hand, they indicate that all pellets collapse at low pH, pointing at the acid sensitivity of the ZIF-8 composite materials, while on the other hand, under basic conditions certain composite materials did not dissolve in the aqueous solutions. This could be observed in particular with pellets containing binders PVF or PS. Among the different composite materials, ZIF-8/PVF pellets (formulated with DMF as solvent) clearly showed the best acid/base resistance. In addition, although Park et al. [29] highlighted that the ZIF-8 MOF exhibits a remarkable chemical stability, our commercial sample seems to completely dissolve in solutions of acetic acid (not shown). This may suggest a limitation of the ZIF-8 adsorbent for its use in the adsorptive recovery of products from ABE fermentation broths, where organic acids, like acetic acid, are produced by the micro-organisms prior being converted into the end-products [18-20]. Since fermentation broths have rarely a pH inferior to 4.5, as it results in the cell death of the micro-organisms [18-20], Figure 5 (left) suggests that the ZIF-8 composites could resist real fermentation conditions. From the hydrothermal stability test, PVF as a binder, also consistently with the other stability assessments (Fig. 5, right), results in (the most) resistant pellets. The stability tests suggest that CA could also be considered as an appropriate binder. In addition, Figure 6 reveals that the ZIF-8 material formulated with the PVF binder has an excellent long-term stability, where the adsorption properties did not change over an extended period of 3 years.
Figure 5. Left) Acid/base stability of ZIF-8 pellets, in ammonium hydroxide and acetic acid solutions with varying pH (submerged overnight at room temperature). Right) Hydrothermal stability of ZIF-8 pellets contacted with hot water (353 K) for 4 hours. Pellets were made with DMF and a binder fraction of 15 wt%. The scale of Fig. 5 left should not be compared with those of Fig. 5 right.

In summary, although the stability tests are based on a rather rudimental approach, they nevertheless give a simple way to identify potential recipes. This work points out that the PVF binder is the best choice for producing resistant ZIF-8 pellets. Further improvement of the formulation method is, however, required, because the pellets remain brittle and a large amount of material is lost due to crushing with the ECS approach. Other approaches, such as phase inversion [30-32], will be explored with the PVF binder recipe identified in this work. Furthermore, from a practical point of view, the reusability of the materials subjected to a cyclic contact with real fermentation broths or model solutions, in several adsorption-desorption/regeneration cycles, will also be inspected in further studies.

Figure 6. Long-term stability of ZIF-8 materials. Adsorption equilibrium of EtOH vapor at 323.15 K on ZIF-8 powder and composite pellets after storage for 3 years. (○) ZIF-8 powder fresh, (▲) ZIF-8/PVF fresh and (△) ZIF-8/PVF 3 years stored (15 wt% binder and DMF as solvent).
3.4. Breakthrough curves.

The separation performance of the ZIF-8 (composite) materials was assessed by pumping a model solution, containing acetone (1 wt%), n-butanol (2 wt%) and ethanol (0.5 wt%) diluted in water, at 0.5 ml/min and 298 K, through columns packed with pellets. The ZIF-8/PVF composite material was compared to the binder-free pellets as well as to pellets containing PVC and PEI. The results of the breakthrough experiments are shown in Figure 7. All composite materials can clearly separate the three components from each other, with 1-butanol, acetone and ethanol eluting at different times from the columns. As expected, 1-butanol elutes the latest, adsorbing preferentially over ethanol and acetone [3-4]. Similar to our previous works [3-4], the breakthrough curve of acetone also exhibits an overshoot, proving that acetone is readily adsorbed, but pushed out of the ZIF-8 pores and concentrated by the 1-butanol front. Furthermore, the difference in elution profile sharpness for acetone, ethanol and n-butanol is related to the stepped isotherm shape [17].

![Figure 7](image_url)

**Figure 7.** Breakthrough curves of (○) ethanol (0.5 wt%), (▲) acetone (1 wt%) and (×)1-butanol (2 wt%) diluted in water on ZIF-8 packed beds, containing binder-free pellets or pellets with PVF, PEI or PVC as binder (circa. 15 wt% and DMF as solvent) at 293 K and a flow rate of 0.5 ml/min. All graphs have the same scale.

The comparison of the binder-free pellets with those containing binder shows that various features of the breakthrough curves are altered by the formulation. First, the average breakthrough times of all components are shifted to the left, indicating that they are less adsorbed per unit volume. The amount n-butanol adsorbed on the ZIF-8 binder free pellets was 0.274 g/g, while for the polymeric MOF materials being 0.252, 0.217, 0.239 g/g for ZIF-8/PEI, ZIF-8/PVC and ZIF-8/PVF, corresponding to a decrease of 8, 21 and 13%, respectively (see Methods
for more detail). This decrease is attributed to the presence of the binder and follows the same trend as the amount of binder in the material estimated by EDX analysis (see Table 1). Differences in results, may, however, originate from the sample size. While breakthrough experiments are performed on a large amount of particles, the characterization measurements are typically carried out only with a handful amount of particles. Second, as a result, the overshoot of acetone is also less pronounced. And, third, the breakthrough curves are broader for the composite materials than the binder-free pellets. The broadening of the elution profiles typically originates from unfavorable mass transfer [5]. Here, under flow conditions, the binder apparently leads to an additional diffusion resistance, compared to the unformulated ZIF-8 material. Such an effect was not observed in the vapor adsorption experiments (see Fig. 3, right). This is corroborated by the porosimetry measurements (see Table 1 and Fig. 8), which give information on the average particle size (d_{particle, 50}), the material density (\(\rho\)), the total porosity (\(\nu_{tot}\) in g/ml and %), the average (macro-) pore size (d_{pore, avg}) as well as the micro-porosity (\(\nu_{micropore}\)) and total (micro- and meso-) porosity (\(\nu_{tot,m}\)). They indicate that the composite materials are more porous and possess more large pores than the binder-free materials (Table 1) as well as having narrower pore size distributions (Fig. 8, middle), while preserving access to the micropores and possessing similar particle size distributions (Fig. 8, left and right).

Table 1. EDX, mercury and argon porosimetry results

|       | EDX binder (%) | Hg d_{particle, 50} (\(\mu\)m) | Hg \(\rho\) (g/ml) | Hg \(\nu_{tot}\) (ml/g) | Hg \(\nu_{tot}\) (%) | Hg d_{pore, avg} (\(\mu\)m) | Ar \(\nu_{micropore}\) (ml/g) \(|^a|\) | Ar \(\nu_{tot, m}\) (ml/g) \(|^a|\) |
|-------|----------------|-------------------------------|-------------------|------------------------|----------------------|-----------------------------|-----------------------------|-----------------------------|
| Binder-free | 0              | 445                           | 0.6194            | 0.832                  | 51.54                | 0.292                       | 0.460                       | 0.687                       |
| PEI    | 14.2 ± 0.8\(^a\) | 414                           | 0.4763            | 1.2                    | 59.94                | 1.514                       | 0.386                       | 0.570                       |
| PVC    | 22.7 ± 1.0\(^a\) | 397                           | 0.5009            | 1.064                  | 61.13                | 1.300                       | 0.340                       | 0.506                       |
| PVF    | 20.4 ± 0.3\(^a\) | 360                           | 0.5372            | 0.977                  | 60.48                | 0.913                       | 0.383                       | 0.560                       |

\(^a\) standard deviation
\(^b\) at 0.2 p/p_0
\(^c\) at 0.95 p/p_0

Figure 8. Particle size (left) and pore size distributions (middle), obtained from mercury porosimetry, and Ar isotherms at 87 K (right) of binder-free pellets and pellets containing 15 wt% binder (i.e. PVF, PVC or PEI, and DMF as formulation solvent). The comparison between the ZIF-8 powder and binder-free pellets can be found elsewhere [17].

Thus, the binder acts as a diffusion barrier for a liquid mixture, which could not be observed under vapor phase conditions. Differences in molecular diffusion of a liquid compared to vapor, the need of co-diffusion with
water, ethanol and acetone into the binder layer surrounding the crystals, or, together with, the partial blocking of the ZIF-8 pore entrances may lay at the origin of this macroscopic observation. The correct identification and quantification of mass transfer resistances is a very tedious work [33-35] and lies beyond the scope of this study.
4. Conclusions

The shaping of metal-organic frameworks (MOFs) materials into resistant structures, while maintaining their adsorption and separation performance, is an important aspect towards their implementation into absorptive processes. In this work, a simple extrusion-crushing-sieving (ECS) approach was used to formulate ZIF-8 crystals into resistant pellets. 55 recipes, with different binders, binder fractions, and solvents, were evaluated with a series of stability tests and adsorption and separation experiments. Various recipes were identified to produce resistant pellets, in particular those containing PVF, CA or MC. For the application of absorptive recovery from aqueous mixtures, such as fermentation broths, the stability tests have pinpointed that PVF (polyvinylformal) is a promising binder to generate resistant pellets with ZIF-8 crystals. Adsorption and separation experiments have shown that the ZIF-8 adsorption properties are not altered by the formulation. However, under liquid phase flow conditions, the binder appears to generate an additional (unfavorable) mass transfer resistance. Furthermore, the recipes generated very porous (composite) materials with narrow pore-size distributions. Finally, from this experimental work, besides identifying promising binder recipes, new prospects were also opened up for further investigation, such as the better understanding of the ZIF-8/binder (in)compatibility, the reusability of composite material for several adsorption-desorption/regeneration cycles, the improvement of the ECS approach for reduced loss of material during production, or also the exploration of the additional mass transfer resistance generated by the binder. Further investigation and improvement of these issues need to be considered for the proper design of separations involving such ZIF-8 MOF composite materials.
Conflicts of interest

The authors declare they have no conflicts of interest, nor competing financial interests.

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