surface. In some embodiments, the step of contacting the MOF containing solution with an acoustic reflector surface comprises positioning or otherwise providing the acoustic reflector surface within the MOF containing solution. The acoustic reflector surface is preferably spaced away from the source of the high frequency ultrasound applied within the MOF containing solution that it reflects off the acoustic reflector surface such that a standing wave is formed through constructive interference. In this respect, the reflected sound waves are able to interact with the original transmitted wave. If the reflected and the transmitted wave are in phase, i.e. the peaks and troughs of the waves are aligned, then constructive interference will occur leading to resonance. With this occurrence, pressure nodes and anti-nodes will form along the path of the interacting sound waves at distances equal to multiples of half the wavelength of the waves.

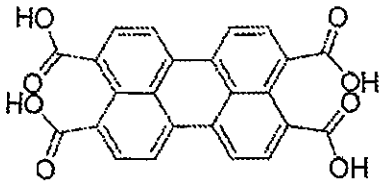
[019] The high frequency ultrasound can be applied or produced from any suitable device. In embodiments, the high frequency ultrasound is applied by high frequency transducer. The high frequency transducer and reflector surfaces are preferably parallel spaced apart within or relative to the MOF containing solution. Again, that spacing is suitable for the formation of a standing wave ~~is formed~~ through constructive interference of the reflected and the transmitted wave (i.e. the reflected and the transmitted wave being in phase).

[020] In some embodiments, the present invention provides a method of separating a metal organic framework (MOF) from a solution, comprising:

providing a MOF containing solution in a housing containing a high frequency transducer and an acoustic reflector surface, the transducer and the acoustic reflector surface being spaced apart within the housing such that a standing wave is formed through constructive interference; and

operating the transducer to apply a high frequency ultrasound of at least 20 kHz to the MOF containing solution;

thereby substantially separating the MOF from solution as an aggregated sediment which settles out of the MOF containing solution, leaving any trapped ligands, metal salts or contaminants in solution.



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wherein X is hydrogen, -NHR, -N(R)$_2$, halides, C_{1-10} alkyl, C_{6-18} aryl, or C_{6-18} aralkyl, -NH_2, alkenyl, alkynyl, -Oalkyl, -NH(aryl), cycloalkyl, cycloalkenyl, cycloalkynyl, -(CO)R, -(SO_2)R, -(CO_2)R, –SH, -S(alkyl), -SO_3H, -$SO_3^{3-}M^+$, -COOH, -COO^-M^+, ~~-PO_3H_2-~~ -$PO_3H_2^-$, -$PO_3H^-M^+$, -$PO_3^{2-}M^{2+}$, or –$PO_3^{2-}M^{2+}$, -NO_2, -CO_2H, silyl derivatives; borane derivatives; and ferrocenes and other metallocenes; M is a metal atom, and R is C_{1-10} alkyl.

[047] In one embodiment, the multidentate linking ligand comprises a ligand having formula 3 previously described. In another embodiment, the multidentate linking ligand comprises a ligand having formula 18 ("BTB"). In a further embodiment, the multidentate linking ligand comprises a ligand having formula 14.

[048] A second aspect of the present invention provides an apparatus for separating a metal organic framework (MOF) from a MOF containing solution, comprising:

a housing having a reservoir capable of receiving a MOF containing solution;

a high frequency ultrasound transducer operatively connected to the reservoir and capable of applying frequencies of at least 20 kHz, preferably between 20 kHz to 4 MHz, more preferably 500 kHz to 2 MHz, more preferably between 800 kHz and 2 MHz, and yet more preferably between 1 MHz and 2 MHz to the MOF containing solution; and

an acoustic reflector surface spaced apart from the transducer within the housing, the transducer, in use, being operated to reflect said applied high frequency ultrasound off the acoustic reflector surface, said acoustic reflector

photograph of one 2000 kHz plate transducer used in the reactor set up shown in (a); and c) a schematic of a standing wave pattern formed by the superimposition of a reflected sound wave within the megasonic separator shown in (a).

[077] Figure 3A provides three photographs of solution being treated in the separator shown in Figure 2C at specific times (1 minute, 4 minutes and 10 minutes) during a process according to one embodiment of the present invention.

[078] Figure 3B provides a comparison of SEM images of (a) and (b) Al-fum; (d) and (e) MIL-53 using conventional centrifuge separation on the left and megasonics on the right; (f) and (g) Comparison of the XRD pattern diffraction of the megasonic and centrifuge product compared to a calculated pattern for Al-fum and MIL-53 respectively.

[079] Figure 3C provides a thermogravimetric analysis of Al-Fumarate and MIL-53 (Al) (heating rate: 5 °C/min).

[080] Figure 4A provides a photographic comparison and a comparison plot of the backscattering and transmission data of the supernatant collected from the first separation of the MOF containing solution using centrifuge and applied frequencies (megasonic) for (A) Al-Fumarate supernatant; and (B) MIL-53 (Al) supernatant.

[081] Figure 4B provides representation of BET surface area, ~~SABET~~ SA_{BET} showing the difference between the product isolated with megasonic and centrifuge for (a) Al-fum; and (b) MIL-53, respectively.

[082] Figures 5 and 6 shown the experimental set up of a second separator set-up with a high frequency system according to an embodiment of the present invention.

[083] Figure 7 provides a plot of obtained supernatant volumes following megasonic separation of Al-Fum MOF for various frequencies. The total volume of MOF containing solution is 500 mL

kept at a temperature from about 25 °C to about 130 °C depending on the MOF synthesis. Typically, higher ligand concentration provides increased yields, however, the risk of blockage in the flow reactor 50 is also increased.

[125] In a typical reaction, two separate solutions of the precursors are pumped through a T-type static mixer to promote diffusion mixing of the reagent input streams. The combined reagent streams are then directed into the heated reactor zone of the Salamander Flow Reactor for a predetermined residence time. On exiting the reactor, the MOF stream 65 is cooled in an external heat sink unit, based on a coiled tube in a water bath (Figure 2B). Then the stream passes through a back-pressure regulator, and is collected for the next process steps. If desired, the solvent can be reused by recycling after the first separation stage. This is particularly attractive for recycling the unreacted ligand which is usually the most expensive reactant, or when an expensive or toxic solvent is used.

[126] MOF stream 65 can be collected in a container or reservoir 70 which can then be subsequently fed into a megasonic separator 100 according to the present invention. This device is illustrated in more detail in Figure 2C.

Synthesis of Al-Fumarate

[127] The general procedure described above was employed. An aqueous solution of 0.35M $Al_2(SO4)_3$ $18H_2O$ and an aqueous solution of 0.7M of fumaric acid and 2M of NaOH solution were mixed under continuous flow conditions and heated in a tubular reactor. The synthesis was conducted at 65 °C using a total flow rate of 90 mL•min^{-1}, giving a total residence time of 1.2 min. The material was washed three times with fresh water and twice with ethanol and dried in vacuum (500 mbar) for 8 hours at 40 °C. Yield: 100%.

S2.b. Synthesis of MIL-53 (Al)

[128] The general procedure described above was employed. An aqueous solution of 0.08M ~~$Al(NO)_3$~~ $Al(NO_3)_3$ and an aqueous solution of 0.08M of terephthalic acid and 0.24M of NaOH solution were mixed under continuous flow conditions and heated in a tubular reactor. The synthesis was conducted at 140 °C using a total flow rate of 90 mL•min-1, giving a total residence time of 1.2 min. The

in the range 0 – 120 kPa were measured by a volumetric approach using a Micrometrics ASAP 2420 instrument. All the samples were transferred to pre-dried and weighed analysis tubes and sealed with Transcal stoppers. Al-Fumarate and MIL-53 were evacuated and activated under dynamic vacuum at ~~10-6~~10^{-6} Torr at 140 °C for 8 hours. Ultra-high purity N_2, CH_4, H_2 and CO_2 gases were used for the experiments. N_2 and H_2 adsorption and desorption measurements were conducted at 77K. Surface area measurements were performed on N_2 isotherms at 77K using the Brunauer-Emmer-Teller (BET) model with adsorption values increasing range of 0.005 to 0.2 relative pressures while the CH_4 adsorption and CO_2 adsorption measurements were done at 273 and 298 K, respectively.

EXAMPLE 2 – Investigation into changes in MOF Composition

[140] In order to investigate whether megasonics separation introduces changes in the MOF composition, ζ-potential measurements were recorded after each washing step of Example 1 as shown Table 2.

[141] **Table 2.** ζ- Potential of the Al-Fumarate and MIL-53 MOF material after each wash step using Megasonics using water as a dispersant.

MOF washing process (Megasonics)	**ζ- potential (mV)**
Al-Fumarate flow reactor	+8.3 ± 0.4
Al-Fumarate wash 1 in H_2O	+8.8 ± 0.0
Al-Fumarate wash 2 in H_2O	+8.8 ± 0.1
Al-Fumarate wash 3 in H_2O	+8.9 ± 0.2
Al-Fumarate wash 4 in EtOH	+10.6 ± 0.2
Al-Fumarate wash 5 in EtOH	+11.3 ± 0.8
MIL-53 flow reactor	+13.3 ± 0.4
MIL-53 wash 1 in H_2O	+15.1 ± 0.5
MIL-53 wash 2 in H_2O	+14.7 ± 0.3
MIL-53 wash 3 in H_2O	+12.6 ± 0.5
MIL-53 wash 4 in EtOH	+12.7 ± 0.2
MIL-53 wash 5 in EtOH	+14.6 ± 0.1

[142] No significant changes to the surface charge were observed, pointing to a separation that is based on reversible aggregation.

stand or base 203. A glass valve (sampling valve 204) was attached to the lower vessel opening to allow easy sampling of the solids bed, post separation. A piezoelectric transducer 205 (E 805/T/M Meindhardt Ultrasound Transducer) was positioned at the base of the cylinder, which made a water tight seal with the vessel 202. The transducer 205 was capable of operating are three separate frequencies (578, 860, 1138 kHz) in either pulse or continuous configurations. However only continuous was used for the experiments. Ultrasonic signals were generated using an ultrasonic multi-frequency generator (Meindhardt, not illustrated) and power output could be adjusted to a nominal value between 0 and 100%. The vessel 202 was filled with various volumes of MOF (208 – Figure 6) and a stainless steel reflector 210 (thickness 0.5 cm) was positioned to be in contact with the slurry. The reflector 210 was connected to a steel threaded rod 212 which could move freely through a lid 214, allowing the height of the reflector 210 to be altered. The system also included a cooling jacket 216 which where necessary used a flow of cooling water 218 to cool the mixture contained in the vessel 202.

[149] The power draw of the system 200 was determined using a standard power meter (not illustrated), although obtaining an accurate reading was difficult given the large fluctuations at each frequency. The average power draw of the system 200 at each frequency was determined over a 10 minute period of operation with a measurement taken at each minute interval from the power meter. At the completion of the 10 minute period the average power draw of the system at each frequency was determined. At frequencies of 1138, 860 and 578 kHz the power draw of the system was found to be 399±7, 422±2 and 408±17 W ~~(Fig. x)~~, with the baseline power draw (whilst no ultrasonics were generated) of 84 W. This suggests the transducer's 210 power output for each of the frequencies (1138, 860 and 578 kHz) were 315±7, 338±2 and 324±17 W.

Separation Optimisation

[150] Several parameters were of interest when attempting to optimise the separation of the MOF; these included frequency, and reflector height.

[151] In order to determine the best frequency for MOF separation the megasonics vessel was first filled with 500 mL of clean (pre washed) Al-Fum and a frequency (1138, 860 or 578 kHz) was selected. Megasonics were then applied for a period of 10 minutes at 100% power and a reflector height of 14.5 cm, for the chosen frequency. At the end of the treatment period, the megasonics were switched off and the slurry allowed to freely settle for a period of 15 minutes. Following separation, the supernatant was decanted using a peristaltic pump and the volume was recorded before two solids samples were taken using the solids sampling valve ~~202~~204 (Figure 5). The mass of each of the solids samples was weighed before being dried overnight. The solids fraction (mass of solids per mass of slurry) was determined for each sample in order to characterise the degree of separation achieved. Finally, the process was repeated for the remaining two frequencies. The experiment was then repeated for each frequency without the use of a reflector.

[152] Again the same Al-Fum MOF was left overnight before tests were undertaken to investigate the effect of reflector height. The vessel was filled to heights of 11.5, 14.5, 20.5 and 26.5 cm in succession, with megasonic treatment of 10 minutes at 100% and 1138 kHz. The MOF was once again allowed to settle for a period of 15 minutes before supernatant volume and bed mass fractions were taken in the same way as earlier described.

Activation of MOF

[153] Following separation optimisation, transition was made from clean pre-washed MOF to reactor slurry in order to characterise the effects of the megasonics on both the activation process as well as any changes to the MOFs structure. In order to achieve this, 500 mL of Al-Fum reactor slurry was diluted to a 3 L batch. From this batch 500 mL was added to the megasonics vessel 202 and sonicated for 10 minutes at 100% power output with a frequency of 1138 kHz. At the conclusion of the treatment, the slurry was allowed to freely settle for 15 minutes before a solids sample was taken (8 mL) from the top layer (1 cm) of the bed. A peristaltic pump was then used to remove a total of 100 mL of supernatant. 100 mL of fresh water (milliQ grade) was added to the vessel prior to removal of the slurry from the megasonics vessel 202. The slurry was

stirred briefly and a small sample (<5 mL) was taken for SEM analysis before being re-added to the vessel 202 for a further treatment. This was repeated until a total of 4 cycles (washes) had been completed. At the conclusion of the final washing stage, additional solids were removed for BET analysis.

[154] As a comparison, 500 mL of the same batch of diluted Al-Fum was centrifuged at 4500 RPM for 5 minutes. A ~~solids~~ small solids sample was taken for XRD analysis prior to the removal of 100 mL of supernatant. This was replaced with 100 mL of fresh water; the separated MOF was agitated before the process was repeated for a total of 4 washes. At the completion of 4 washes, additional solids were removed for the purpose of BET analysis

[155] Post reactor Mil-53 slurry was then used in place of Al-Fum and the same tests were repeated although in this case separation was achieved without initial the dilution (500 mL to 3 L) given its already dilute nature.

Results and Discussion

[156] *Optimal Frequency* - Carrying out treatments at each frequency, the greatest MOF separation (and hence greatest amount of separation) was achieved when treatment occurred with a frequency of 1138 kHz rather than 860 or 578 kHz (Figure 7). This is supported by the obtained mass fractions within the bed which show the highest concentration of MOF present within the bed when 1138 kHz are used. On the other hand, the same experiments performed without the reflector did not achieve separation, which indicates that in order to isolate the MOF the formation of standing waves is required. The standing wave generates regions of minimal pressure (nodes) and maximal pressure (antinodes) within a separation chamber. Due to local acoustic radiation forces, suspended MOF particles migrated specifically towards the regions of minimal pressure (nodes) and maximal pressure (antinodes). This gathering of MOF material enhanced the tendency to form larger aggregates, which then settle at a greatly accelerated rate to the bottom of the separation chamber, where they were collected.

transducer) prior to beginning flow operation, resulting in an increased temperature of the MOF containing solution of 20-25 °C. After this pre-sonication step, flow was initiated by turning on the pumps 316, 317 and opening a drain valve 315 located at the bottom of the vessel 301. The input of MOF containing solution, along with an ice cooling bath 320 located on the sides of the processing region 307, enabled temperature to be maintained within an optimal range for efficient MOF separation and activation of between 20 and 40 °C across the entire process duration. The processed MOF was collected by removing the solution from the drain valve 315A.

[163] Those skilled in the art will appreciate that the invention described herein is susceptible to variations and modifications other than those specifically described. It is understood that the invention includes all such variations and modifications which fall within the spirit and scope of the present invention.

[164] Where the terms "comprise", "comprises", "comprised" or "comprising" are used in this specification (including the claims) they are to be interpreted as specifying the presence of the stated features, integers, steps or components, but not precluding the presence of one or more other feature, integer, step, component or group thereof.

a high frequency ultrasound transducer operatively connected to the reservoir and capable of applying megasonic frequencies of at least 20 kHz to the MOF containing solution; and

an acoustic reflector surface spaced apart from the transducer within the housing, the transducer, in use, being operated to reflect said applied high frequency ultrasound off the acoustic reflector surface, said acoustic reflector surface being spaced away from the high frequency ultrasound transducer such that a standing wave is formed through constructive interference.

20. A apparatus according to claim 19, wherein the applied high frequency ultrasound is between 20 kHz to 4 MHz, preferably 500 kHz to 2 MHz, more preferably between 800 kHz and 2 MHz, and yet more preferably between 1 MHz and 2 MHz.

21. An apparatus according to claim 19 or 20, wherein the housing comprises a container including at least one wall position to contact the MOF containing solution, and the transducer is high frequency ultrasound transducer is position within the reservoir or in engagement with the at least one wall.

22. An apparatus according to any one of claims 19 to 21, wherein the acoustic reflector surface is generally located in front of the transducer, and spaced apart from that transducer.

23. An apparatus according to any one of claims 20 to ~~2422~~, wherein the high frequency ultrasound transducer comprises a plate transducer.

24. An apparatus according to any one of claims 19 to 23, wherein the housing includes at least one reflector surface designed to reflect the applied megasonic frequencies within the reservoir.

25. A method according to any one of claims 1 to 18 using an apparatus according to any one of claims 19 to 24.