Green Synthesis of a Metal-Organic Framework Selective Towards the Binding of Methylene

Blue

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Abstract

In the summer of 2010, the U.N. deemed that all humans had a right to water, and access to fresh drinking water is a requirement to fulfil other rights. However, millions of people across the globe still live without access to clean drinking water. Shifting weather patterns due to climate change are making access to fresh water even more difficult for some areas, so their reliance on wastewater treatment facilities will only grow if water demands are to be met sustainably. Unfortunately, there exists a class of chemicals known as emerging organic contaminants (EOCs), which easily pass through the filtration systems of conventional wastewater treatment facilities. However, another class of materials known as metal-organic frameworks (MOFs), can be used in junction with classical filtration systems to selectively bind and remove EOCs from the wastewater. The synthesis of MOFs often requires the use of harsh solvents and prolonged use of elevated temperatures. In this work, two MOFs, MIL-53 and NH_2-MIL-53 are synthesized in water at room temperature, and for the first time, sodium bicarbonate is used as a deprotonation agent. The absorption capabilities the latter MOF has of Methylene blue, a potent EOC, are analyzed as an application. Following the synthesis method provided in this work, a range of MOFs could be synthesized without the need for harsh solvents and at room temperature, substantially increasing the green characteristics of the synthesis.

Introduction

On July 28th, 2010, through Resolution 64/292, The United Nations General Assembly formally recognized human's right to water, while also acknowledging that access to sanitation and clean drinking water were vital backbones to all other human rights[1]. However, there exists

at least 884 million people globally and 2 million United States citizens that still live without access to clean drinking water[2,3]. To make matters worse, climate change is causing weather patterns to shift, and many areas are receiving far less rainfall on average leading to longer and more intense droughts[4]. Domestically, this is seen throughout the Western third of the country, as of April, 2021 nearly 95% of the area is under some form of drought[5]. As surface water sources dry up, states have relied heavily on groundwater pumping to meet demands, but even this source will eventually run dry if substantial, prolonged rainfall does not return to the area[6].

Wastewater collection and remediation technologies will have to be utilized at a much more efficient rate if climate patterns continue to cause the further aridification of certain areas. Conventionally, when wastewater is collected and transported to a remediation facility, solids and particulates are first removed through coagulation, flocculation, and sedimentation. The now particle-free solution is filtered through layers of sand, gravel, and charcoal of varying pore sizes to remove the dissolved contaminants[8]. This process is sufficient at removing a majority of the dissolved contaminants, but some are not adsorbed strongly enough by the oxides and hydroxides of the filtration layers to be pulled out of solution. These will then end up in the "clean" water, and if that water is returned back to environment or to peoples taps it can cause further contamination even after remediation. Emerging organic contaminants (EOC's), a classification of chemicals ranging from pharmaceutical compounds to organic dyes, are notorious for their ability to pass through conventional water remediation processes[9]. Though these compounds are generally in low concentration, modern water treatment facilities have implemented an ozonation stage in the remediation process in an effort to oxidize and remove the EOCs, but even this has proven to be ineffective for several contaminants[7]. For instance, an estimated 40 million United States citizens, over 10% of the population, are exposed to

pharmaceutical drugs in tap water simply due to others flushing prescription drugs down the toilet[10].

      To address this issue, researchers have turned their attention to the implementation of metal-organic frameworks (MOFs) in the filtration system. These structures, first studied in the 1990s, are the 1-D, 2-D, or 3-D molecular self-assembled product when a metal center and organic linker are combined in solution, and are most famously known for their crystallinity, porosity, and extreme surface areas[11]. They form when the open binding sites of the inorganic centers accept electrons from the organic linker molecule in a repeatable, systematic way. This gives them superior variability as nearly any combination of materials can be turned into a MOF when ideal synthesis conditions are achieved[12]. The most useful aspect of these materials, however, may be the fact that the mere addition of a functional group to the organic linker, creates two entirely different MOFs with their own unique characteristics. This is exemplified in Scheme 1a and 1b which shows the formation of two distinct MOFs, with the only difference being the addition of a functional group on the organic linker in 1b. This extreme tunability MOFs possess has led to numerous applications including gas sorption, separation, and storage, catalysis, delayed drug release, environmental decontamination[13], etc.
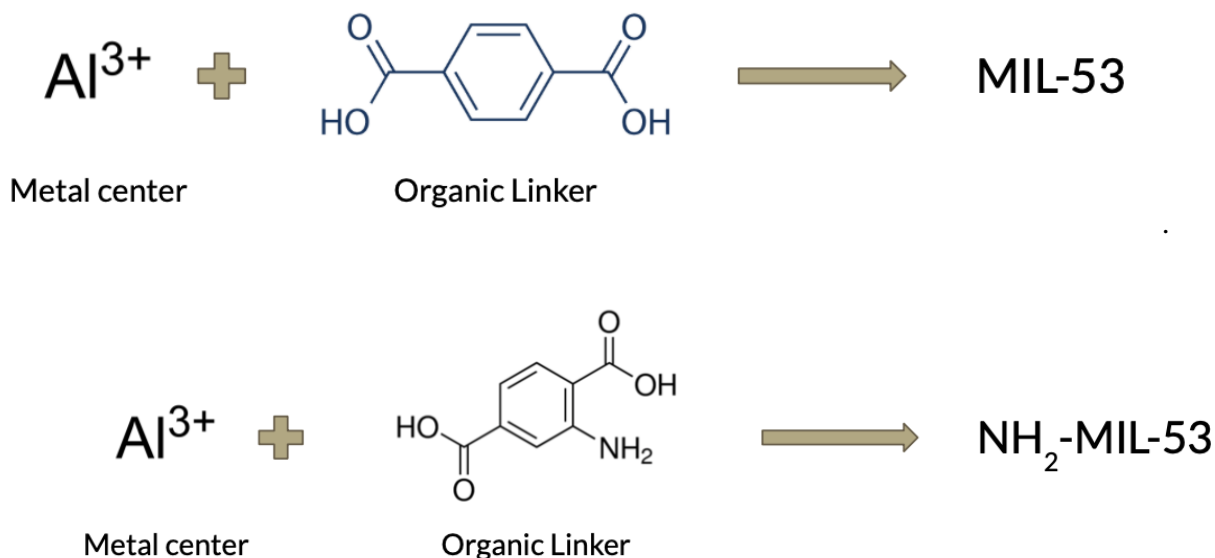
Scheme 1: Formation of a MOF known as MIL-53 in (a) (upper), and NH$_2$-MIL-53 in (b) (lower). Although the two MOFs are only differentiated by a singular functional group on the organic linker, they have vastly different properties.

Pharmaceutical contamination, as eluded to earlier, is not the only EOC-type contamination currently being found at wastewater remediation facilities. Recently, larger concentrations of cationic dyes have been found in wastewater due to quickly-developing dye-related industries. These compounds, even though they are still generally found in very small concentrations, threaten human health and environmental safety as many are potent toxins and carcinogens[14]. An organic dye of particular interest, called methylene blue (MB), has several classical applications including medicinal and surgical uses. It is a cationic molecule that is stable in water at room temperature, but is a potent EOC as it is often missed by conventional wastewater remediation techniques[15]. In an attempt to synthesize a material that can bind an remove dissolved MB from water, a research group studied the binding selectivity of the MOF shown in **scheme 1a** towards the dye[16]. This material, denoted MIL-53(Al), is classically

synthesized via a hydrothermal reaction between aluminum nitrate and 1,4-benzenedicarboxylic acid (terephthalic acid)[17]. By itself, the MOF showed very poor adsorption of aqueous MB (only 5 milligrams of dye adsorbed per gram of material), but when the terephthalic acid linker was functionalized with an amino group, as seen in **scheme 1b**, the adsorption of MB increased by nearly 10-fold[16]. This speaks to the variability and versatility of MOFs, as the simple act of modifying the linker with a single functional group increased the adsorption capabilities drastically.

Once the analyte is adsorbed to the MOF, it is crucial that it can easily be desorbed to regenerate the starting material. For NH$_2$-MIL-53, it was found that MB was easily desorbed by washing the adsorbed material with a solvent solution of 40% methanol and 60% acetonitrile[18]. The dye-containing solvent could then be evaporated off, leaving just the MB behind where it could then be properly disposed. However, there has been a recent push through the scientific community to shift their lab practices to better fit the guidelines of "green chemistry". Developed by Paul Anastas and John Warner, the 12 green chemistry principles strive to reach sustainability in the chemistry lab while meeting environmental and economic goals[19]. Some of the guideline principles relevant to this work include: less hazardous chemical syntheses, safer solvents and axillaries, and design for energy efficiency. An example of making a reaction "greener" would be the substitution of a strong acid/base like hydrochloric acid or sodium hydroxide with something milder like acetic acid or sodium bicarbonate, or the replacement of a harsher solvent like dichloromethane or dimethylformamide (DMF) with something drain-safe like water or ethanol.

This "green" analysis can be applied to any experimental methods by simply using the 12 principles as guidelines, allowing researchers to identify potentially inefficient or non-

environmentally friendly methods. This extends to the synthesis of MIL-53, which when comparing the conventional synthesis of the material to the 12 principles, looks quite "non-green". For instance, the classical hydrothermal synthesis route used by most researchers studying the material not only uses dimethylformamide (DMF) to dissolve terephthalic acid, it requires heating the solution at 220 °C for 72 hours[17]. DMF is used as it a polar aprotic solvent that has the unique capability of dissolving both organic and inorganic substances, while also containing some catalytic properties. However, DMF poses several threats to human health, especially if accidentally mixed with an acid or base[20]. DMF is also not drain safe. When analyzing the heating aspect of the reaction, it is clear that a significant amount of electricity must be used to keep the reaction heated for that length of time. Just by considering these two aspects of the classical synthesis of MIL-53, it is clear that there is plenty of room to increase the green characteristics of the reaction.

Some research groups have already begun increasing the "greenness" of the synthesis of MIL-53. For instance, one group found by mixing the organic linker in with a 1:2 ratio with sodium hydroxide, the acid could be fully deprotonated, allowing it to be solubilized in water[21]. Amazingly, when this solution was combined with a solution of aluminum nitrate, the MOF self-assembled at room temperature. This simple modification of the reaction not only reduced the need for a harsh solvent like DMF, it completely eliminated the need for the lengthy heating phase. Although this reaction does introduce a strong base, if the terephthalic acid is used in a slight excess during the deprotonation phase, theoretically all of the base could react, meaning everything leftover could be simply washed down the drain. There is still room to grow for this reaction, as it could theoretically be possible to create the deprotonation of the acid with a weak, drain-safe base like sodium bicarbonate. Otherwise known as baking soda, this compound reacts

with a base to form water and carbon dioxide, depicted in **Figure 1**, which bubbles out of the reaction vessel, driving the deprotonation forward[22].

Figure 1: Reaction of sodium bicarbonate and acetic acid creates carbon dioxide gas

Many metal-organic materials have shown high uptake of aqueous methylene blue, but their syntheses often include the use of harsh solvents and elevated temperatures for a significant duration of time[23-24]. While it is crucial EOCs like MB are removed from remediated wastewater, it is also important that the synthesis of the materials capable of doing the job is not significantly detrimental towards the environment. The green synthesis and application of MOFs selective towards cationic dyes has been grossly under-studied, which is exactly what the scope of this work intends to do.

Methodology

Synthesis of MIL-53 via sodium hydroxide:

This research project began by trying to qualitatively recreate the synthesis of MIL-53 with the use of sodium hydroxide as a deprotonation agent. To begin, a just under a 2:1 molar ratio of sodium hydroxide to terephthalic acid was combined in a beaker, with strong stirring. The reaction was allowed to proceed until it seemed no more of the solid terephthalic acid was

dissolving into the reaction solution. The remaining terephthalic acid was filtered off, and the clear solution was collected for future use. While the terephthalic acid reacting with the sodium hydroxide, a solution of aluminum nitrate was prepared in a separate beaker, ensuring the concentration of aluminum cations was in molar equivalence with the terephthalic acid in the other beaker.

Once the aluminum and terephthalate solutions were prepared, they were combined into a new beaker with stirring where an immediate white precipitate formed upon contact of the two solutions. This reaction was allowed to continue overnight, where it was then filtered and the precipitate was washed with a mild base to ensure no terephthalic acid or aluminum nitrate remained trapped in the pores. The solid was placed on a watch glass and put in the oven at 80°C to remove any remaining solvent. The product MIL-53(Al) was characterized via IR spectroscopy, thermogravimetric analysis, and powder x-ray diffraction.

Synthesis of MIL-53 via sodium bicarbonate:

The qualitative synthesis of MIL-53 via sodium bicarbonate was almost identical as the synthesis route using sodium hydroxide. A slightly less than 2:1 molar ratio of sodium bicarbonate to terephthalic acid was combined in a beaker. However, this time the reaction was allowed to proceed until the formation of carbon dioxide bubbles ceased. The undissolved terephthalic acid was filtered off, and the solution combined with a 1:1 molar equivalent solution of aluminum nitrate. Likewise, a white solid formed immediately, and was filtered, dried, and characterized in the same manner as the hydroxide route. Once it was proven that this synthesis route actually formed MIL-53 (analyzed in the discussion), the same synthesis route would be

used to attempt to make NH_2-MIL-53, which has a significantly higher affinity for MB in solution.

Synthesis of NH_2-MIL-53:

Like mentioned previously, once it was proven that the sodium bicarbonate route was successful at synthesizing MIL-53 with aluminum nitrate and terephthalic acid, the same synthesis strategy, albeit quantitatively this time, was extended and used instead to deprotonate 2-aminoterephthalic acid. One gram of the acid was combined with just under two molar equivalents of sodium bicarbonate, and allowed to proceed until carbon dioxide bubbles ceased to form. The yellow solution was filtered off until it was completely transparent, and once again combined with a 1:1 molar equivalent solution (about one gram) of aluminum nitrate. The pale-yellow solid was filtered, dried, and characterized in the same manner as mentioned above. The reaction produced 0.754 g of NH_2-MIL-53, or equivalent to a 72% reaction yield.

Methylene blue adsorption studies of sodium bicarbonate synthesized NH_2-MIL-53:

To compare the MB adsorption quantities of the green-synthesized NH_2-MIL-53 to those reported in the literature, a standardization curve relating the concentration of MB to its absorbance at 665 nm was prepared. This was done by preparing a 50 mg/L solution of MB in a 200 mL volumetric flask, and quantitatively transferring 50 mL of the subsequent homogenized solution into a 100 mL volumetric flask. The flask containing 50 mL of the 50 mg/L solution was diluted to the line, cutting the concentration of MB in that flask to 25 mg/L. This process was repeated six more times, with the final flask containing an MB concentration of just 0.39 mg/L. The absorbances of each standard concentration was recorded in a UV-vis spectrophotometer,

with all of the solutions with an absorbance value of <1.0 at 665 nm used to create the relationship between absorbance and concentration. Since the concentration gap between 3.13 mg/L and 1.56 mg/L was relatively larger than all other gaps, another standard MB solution of 2 mg/L was prepared, and its absorbance used in the standardization curve.

Once the curve was made with a reasonably high R^2 value, 10 mg of the green-synthesized NH_2-MIL-53 was combined with 10 mL of each standard MB concentration in a 10 mL Erlenmeyer flask. The solutions were covered with parafilm, shaken for one minute, and allowed to settle for 30 minutes. Once the 30 minutes had passed, an aliquot of each concentration was removed using a pipet, ensuring no NH_2-MIL-53 came with it. The absorbance at 665 nm for each aliquot was collected, and then they were all returned to their proper Erlenmeyer flasks. This was again repeated after one day, two days, and one week. The now MB-NH_2-MIL-53 material of the highest concentration sample (50 mg/L) was filtered out of solution and dried. The material was again characterized using IR-spectroscopy, thermogravimetric analysis, and powder x-ray diffraction to compare to the dye-free NH_2-MIL-53.

Desorption of methylene blue from NH_2-MIL-53:

To desorb the MB from NH_2-MIL-53, a stock solution consisting of 40% methanol and 60% acetonitrile was prepared. Glass wool was placed into the tip of a long stem glass pipet, which was followed by placing the dye-MOF material on top of it. All of the contents were then compacted into the tip of the glass pipet, and subsequently washed with the stock solution. The solution was allowed to flow through the material, and just before it all had passed through it was topped off until 25 mL of the solution had been used in total. Then, the material was taken out of the pipet, and placed in a 50 mL beaker to which more of the stock solution was added to desorb

the dye from the MOF. All of the solution that came in contact with the MOF was collected and roto-evaporated once the experiment had finished to isolate the MB. The now dry MB was dissolved in 10 mL of deionized water, and the concentration of the solution was found using UV-Vis spectroscopy. The final amount of dye desorbed from the MOF was calculated.

Results/Discussion

Synthesis of MIL-53 via sodium hydroxide:

The first step in this entire research project was to attempt the MIL-53 synthesis strategy first reported by Sanchez et al. in 2015 when they used sodium hydroxide to solubilize and deprotonate terephthalic acid in an aqueous environment. This was a major step towards the greener synthesis of MOFs, as it completely removed the need of DMF to dissolve the protonated acid. The first departure this research took from what has already be recorded in the literature was using a molar ratio of just under 2:1 of sodium hydroxide to terephthalic acid. This was done for two reasons. The first was to prevent the presence of any excess hydroxide ions from being in solution, as if some were present when the aluminum solution was added, aluminate ions could form[25]. When it was assumed the base had fully reacted, pH paper confirmed that the pH of the solution was at 7, meaning very little/no hydroxide remained. The slight under usage of hydroxide was also done to simplify the byproducts of the reaction. If all the hydroxide had reacted, the only solutes in solution should be the terephthalate anions and sodium cations, which is shown in **scheme 2.**

$$C_6H_4(CO_2H)_{2(aq)} + 2\ NaOH_{(aq)} \rightarrow C_6H_4(CO_2)^{2-}_{2(aq)} + 2Na^+_{(aq)} + 2H_2O_{(l)}$$
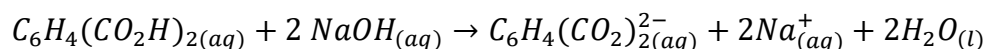
Scheme 2: Neutralization of terephthalic acid. If the terephthalic acid is used in excess, the only solutes remaining after all of the hydroxide reacts away should be terephthalate anions and sodium cations.

As expected, some unreacted acid remained after all of the base was neutralized, which can be seen in **figure 13** in the appendix. This was filtered off and discarded (though it could have been reclaimed to further improve the "greenness" of the reaction), and the terephthalate solution was set aside to begin preparation of the aluminum solution. The exact mass of aluminum nitrate needed to be in molar equivalence with the terephthalate anions was calculated by using the moles of hydroxide added, since it was the limiting reagent in **scheme 2**. The two solutions were combined and allowed to mix according to the methods already mentioned, and after filtering and drying the next steps was to confirm the presence of MIL-53 using spectroscopic techniques.

When analyzing the IR-spectroscopy of the product, there were two major peak shifts expected to confirm the presence of MIL-53. The organic linker, terephthalic acid, contains two carboxylic acid groups, which are well known for producing very broad, generally U-shaped peaks centered around 2500-2600 cm^{-1} (wavenumber). This large, broad peak range of the starting material, which can be seen in **figure 2**, is due to the strong hydrogen bonding that occurs when the acid dimerizes with itself[26]. If the synthesis of MIL-53 was successful, no carboxylic acid peaks would be expected as the acidic hydrogen atoms were removed in the deprotonation phase, preventing any hydrogen bonding from occurring. Secondly, it would be expected that the carbonyl peak (C=O), which is seen in **figure 2** at 1673.90 cm^{-1} would shift to a slightly higher wavenumber. The wavenumber is related to the strength of the bond; a higher

wavenumber means a stronger bond. In the starting material, the oxygen atom in the carbonyl group is interacting with an acidic hydrogen from another molecule. In MIL-53, the oxygen atom would instead be interacting with an aluminum atom. Since aluminum is less electronegative than hydrogen (1.47 vs 2.1)[27], it will not pull on the electrons in the C=O bond as much as a hydrogen atom would. This in turn means there is more electron density in the C=O bond in MIL-53 compared to terephthalic acid, indicating the former has a stronger C=O bond, seeding an expectation that it will be shifted to a slightly higher wavenumber.
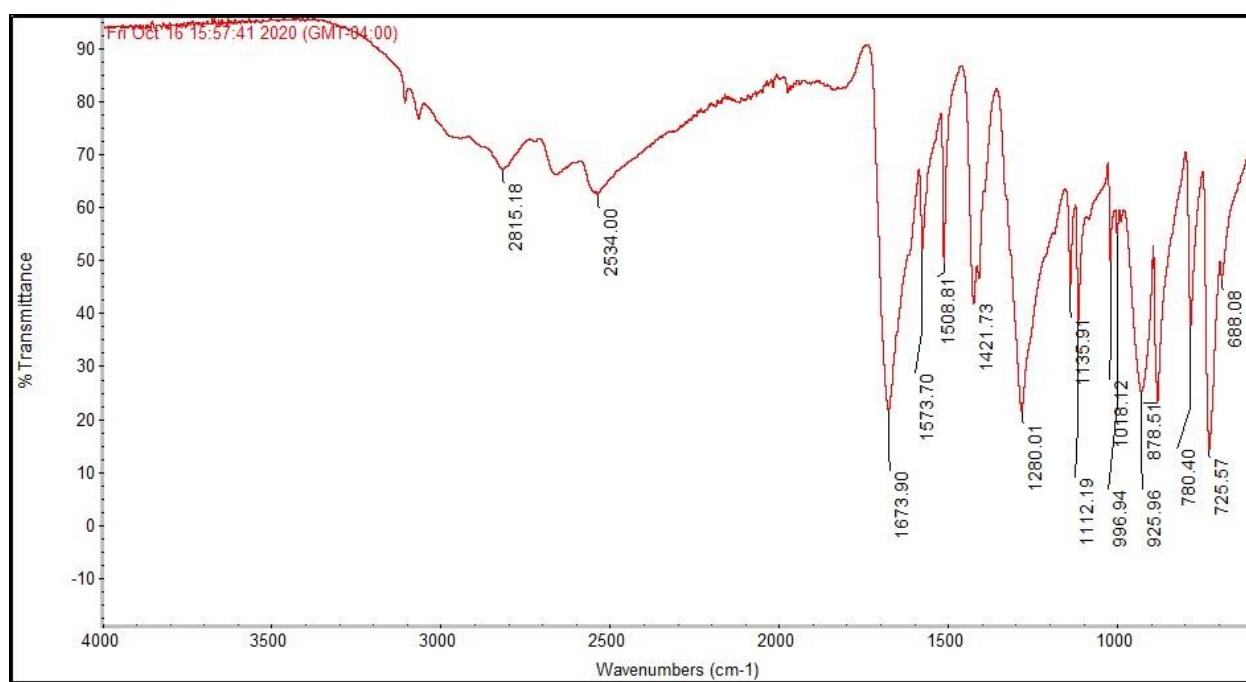
Figure 2: IR spectrum of terephthalic acid. The peak caused from the dimerization of the carboxylic acid groups is very clearly seen between 2000-3000 cm^{-1}.

Figure 3 shows the IR spectrum of the product resulting from the combination of terephthalate anions and Al^{3+} cations. As mentioned above, it was expected **figure 3** would lack the broad carboxylic acid peak, and have a higher wavenumber carbonyl peak. This is exactly what was seen, and even though this alone does not prove the successful synthesis of MIL-53, it proved that no starting material remained from the lack of a carboxylic peak. The carbonyl peak shifted
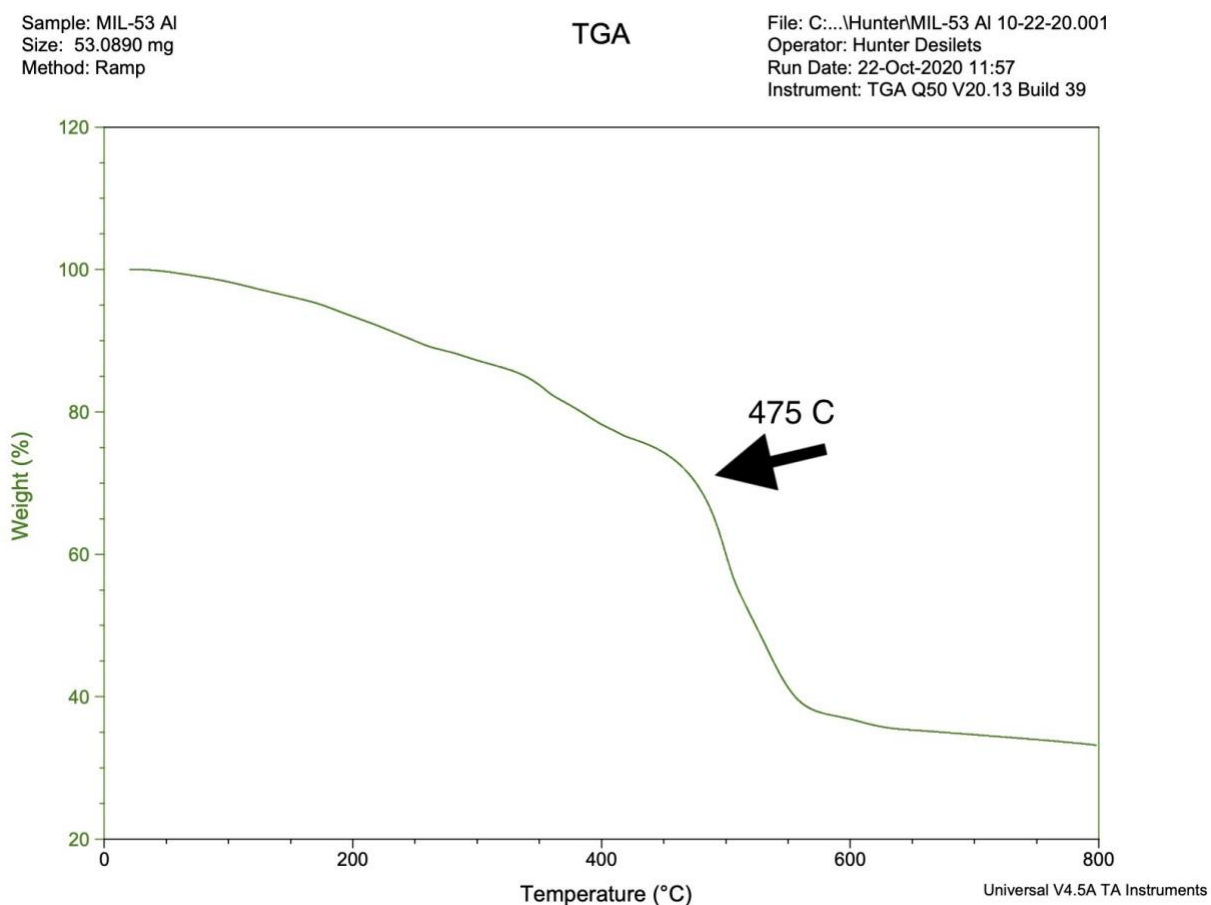
from 1673.90 to 1693.43 cm⁻¹ in the product, indicating the interaction of the oxygen atom with the aluminum. Another important piece of information to mention is that the product had a small peak at 2980.23 cm⁻¹, which is indicative of C=C—H, which was expected as these peaks are due to the aromatic ring in both the starting material and product. The peak is not visible in the starting material due to the broadness of the dimerization peak, but since this peak is not present in the product, the C=C—H peak becomes visible.
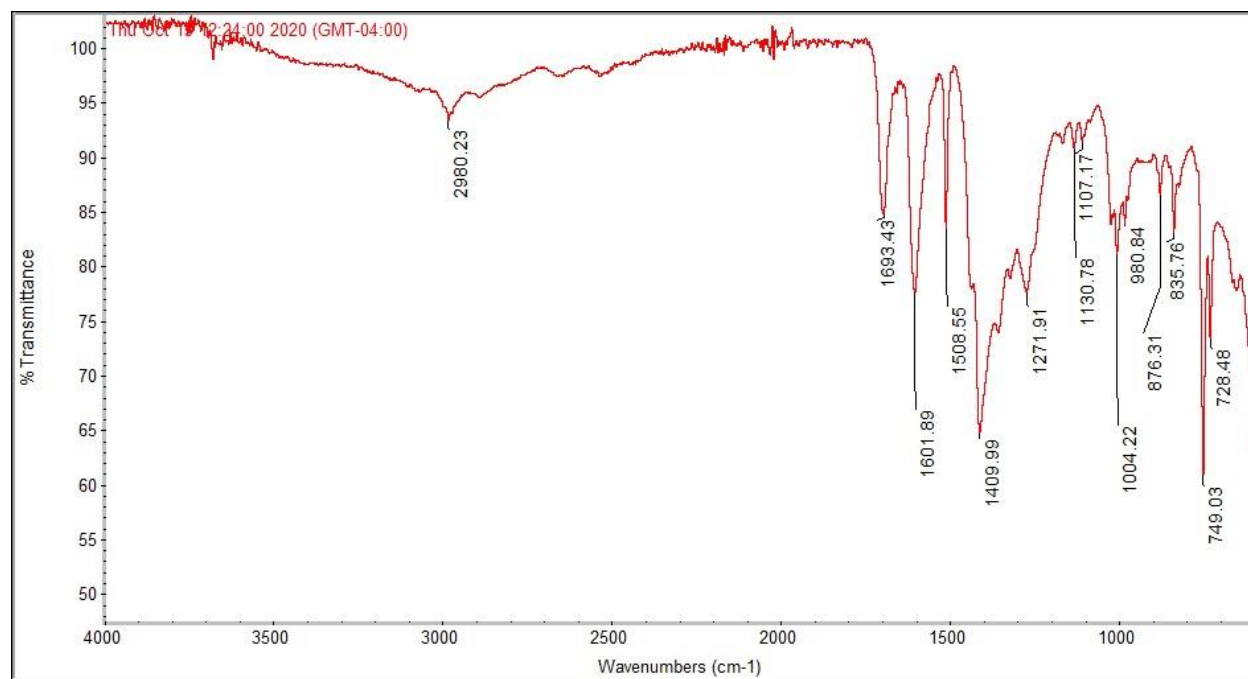
Figure 3: IR spectrum of the product formed when Al^{3+} and $C_6H_4(CO_2)_2^{2-}$ are combined in solution. Notable details include the lack of a carboxylic acid dimerization peak, and a shift to a higher wavenumber in the C=O peak.

After IR, thermogravimetric analysis (TGA) was conducted on the product. This process involves the measurement of weight loss of the material as it is heated at a constant rate. When comparing the collected data to the literature, confirmation of the product can be made if the degradation temperature found on the weight percent vs. temperature plot of the product is similar to that of what has already been published. This is a fine assumption as in theory, it

should not matter which instrument is used, as there should be a constant temperature at which the product degrades. Of course, there will always be slight variations depending on the conditions in which the experiment was run, but as long as it is similar to the literature, it is a step in the right direction. **Figure 4** shows the data recorded from the TGA of the product, which shows a degradation temperature of about 475°C. The literature degradation temperature of the first synthesis of MIL-53 found it to be at 500°C[17], which is a difference of just 5.1%. It is interesting to note the "bleeding" of about 20% mass that occurred between the temperatures of 50-450°C. MIL-53 also readily adsorbs gas molecules from the atmosphere, specifically CO_2[28], so it comes as no surprise that there is a slow release of mass as gas is liberated from the MOF over the temperatures before the degradation of the material.

Sample: MIL-53 Al
Size: 53.0890 mg
Method: Ramp

TGA

File: C:...\Hunter\MIL-53 Al 10-22-20.001
Operator: Hunter Desilets
Run Date: 22-Oct-2020 11:57
Instrument: TGA Q50 V20.13 Build 39

475 C

Universal V4.5A TA Instruments

Figure 4: TGA data of suspected MIL-53. The degradation temperature is similar to the reported literature, being about 5.1% under.

The final form of confirmation used on the product was powder x-ray diffraction. This technique measures the crystallinity of the product, and is a very good identifier as a structure generally diffracts x-rays consistently. Since MIL-53 has had its crystal structure solved and published online, a predicted PXRD spectrum could be made by downloading the CIF file and importing it into a program like CrystalMaker or enCIFer. The collected data vs. the predicted can be seen in **figure 5**. Unfortunately, there is not good agreement between the PXRD of the suspected MIL-53 with the predicted, but it must be remembered that this is only a predicted spectrum. When comparing the spectrum from the product to the spectra published in the literature[16,17], there is good agreement. With the combination of the data from the three spectroscopic techniques, IR, TGA, and PXRD, it was confirmed that this research was able to reproduce the work Sanchez et al., and the next step was to change the base from sodium hydroxide to sodium bicarbonate, with the goal of expanding the green characteristics of MIL-53's synthesis.
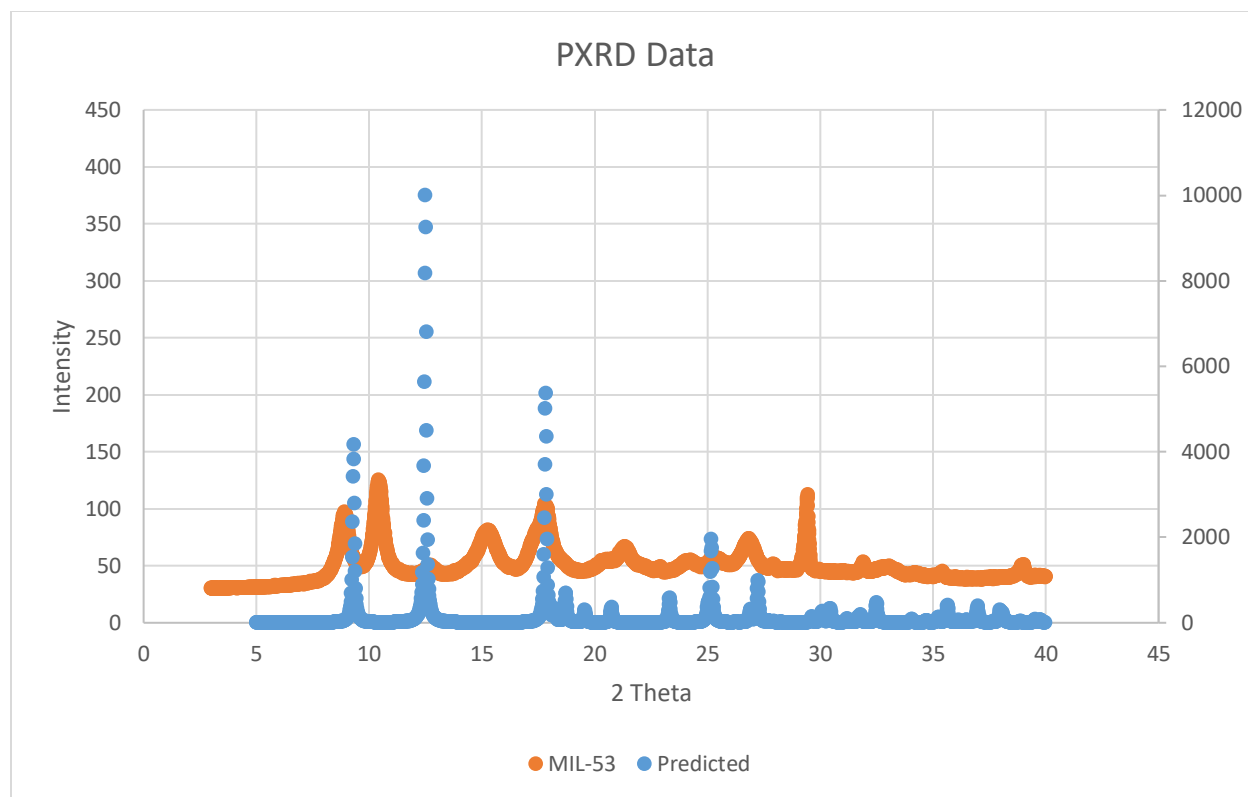
Figure 5: Comparison of the PXRD collected from the suspected MIL-53 to the computer-predicted PXRD of MIL-53. Although they do not look that similar, the data matches well with what has been reported in the literature.

Synthesis of MIL-53 via sodium bicarbonate:

Like mentioned above, the synthesis of MIL-53 was attempted with sodium bicarbonate instead of sodium hydroxide. In the deprotonation phase of the terephthalic acid, it was very important to allow the continuation of the reaction until the formation of CO_2 bubbles ceased. If the reaction would have been stopped short, some base and unreacted acid might have ended up in the beaker unintentionally, leading to the formation of unwanted byproducts. After combination with the aluminum solution, filtration, and drying, IR spectroscopy was similarly taken of the product, which can be seen in **figure 14** in the appendix. If MIL-53 had been made, the same peaks as were aforementioned in the hydroxide-synthesis route would be expected. This

is precisely what was observed, as there was no carboxylic acid dimerization peak, and the carbonyl peak was found within a 2 cm^{-1} difference compared to **figure 3**. This gave good evidence that bicarbonate performed equally as well as hydroxide, but the other spectroscopic techniques were similarly done to confirm the synthesis of MIL-53. **Figure 15** shows the TGA of the bicarbonate product. The spectrum again looks remarkably like that of **figure 4**, so it has been moved to the appendix as well. Finally, **figure 6** compares the PXRD spectra of the hydroxide and bicarbonate synthesis routes. The peaks are remarkably similar, which led to the conclusion that sodium bicarbonate works just as well in comparison to sodium hydroxide in the synthesis of MIL-53.

Figure 6: PXRD spectra of MIL-53 via hydroxide (orange) vs MIL-53 via bicarbonate (grey). The peaks found line up almost exactly, confirming that bicarbonate works in green synthesis of MIL-53.

Synthesis of NH₂-MIL-53:

Once it was proven that MIL-53 could be synthesized by first deprotonating the organic linker with sodium bicarbonate, the same greener synthesis of NH$_2$-MIL-53 was attempted. As of the writing of this, the green synthesis of NH$_2$-MIL-53 via deprotonation had not been attempted in previous research, let alone with sodium bicarbonate as the base. The synthesis strategy used was exactly the same as the last example, with the only difference being the yellow coloring of the organic linker, which now contained an amino group on the aromatic ring. Even though amino groups can act as a weak base, this did not alter the synthesis strategy as amino group is not strong enough to deprotonate one of the carboxylic acids, which would hypothetically create a Zwitterion if it could. 2-amioterephthalic acid, the new organic linker, is still very poorly soluble in water, so the excess material could still be filtered off. Again, when the anionic linker came in contact with the aluminum, a precipitate immediately crashed out, but this time it had a pale-yellow color. Once filtered and dried, the same spectroscopic techniques were used to characterize the powder.
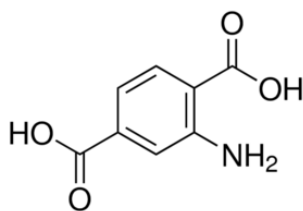
Figure 7: Structure of 2-aminoterephthalic acid. The primary amine substituted on the aromatic ring adds two small peaks between 3300-3500 cm^{-1} in IR spectroscopy.

The IR spectra of the suspected NH$_2$-MIL-53 was predicted to be very similar to that of MIL-53, but with two small peaks between 3300-3500 cm^{-1} to account for the primary amine substituted on the aromatic ring (**figure 7**). The spectra of the product revealed just that, as two peaks not present in **figure 3** were found in **figure 8** at 3383.45 and 3497.45 cm^{-1}, while also

showing the successful deprotonation of the amino-substituted linker (the IR spectrum of 2-aminoterephthalic acid can be seen in **figure 16** in the appendix), and incorporation with the aluminum cations, due to the shift in the carbonyl peak, in the same way previously described for MIL-53.
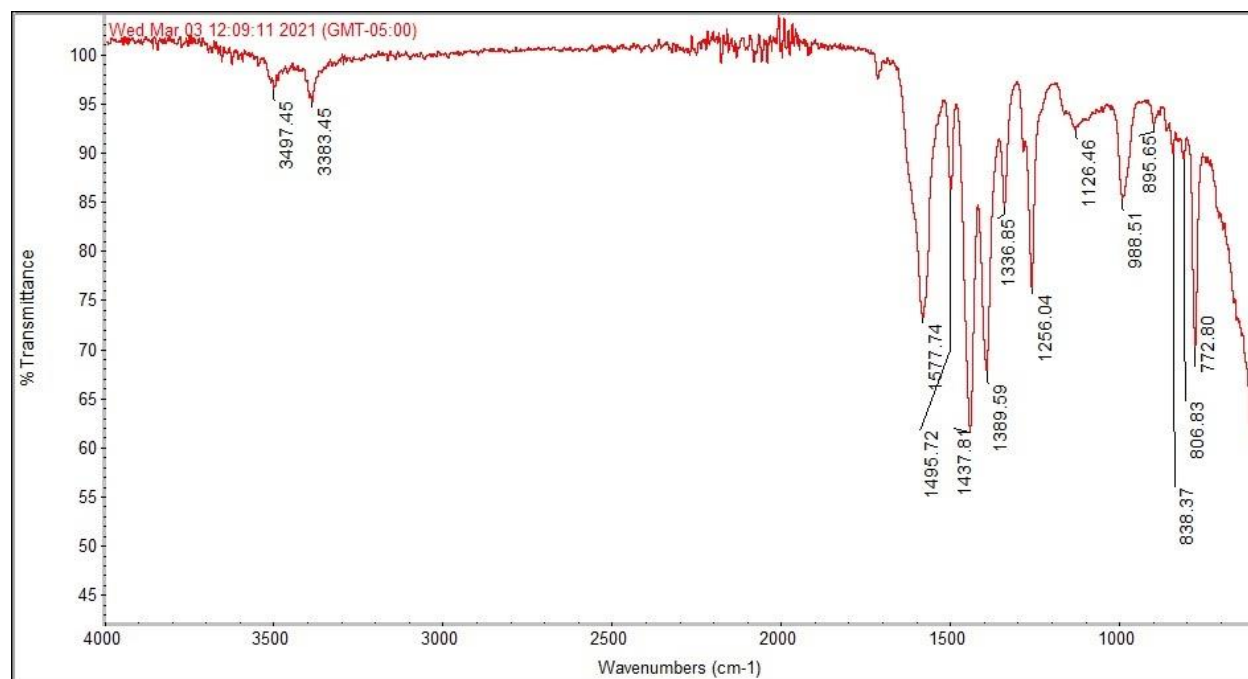
Figure 8: IR spectrum of suspected NH$_2$-MIL-53

Similarly, a TGA of the suspected NH$_2$-MIL-53 was collected, which can be seen in **figure 9**. According to the literature, the decomposition temperature of NH$_2$-MIL-53 is about 450°C, or about 50°C lower than non-substituted MIL-53. **Figure 9** shows the decomposition temperature of the suspected product was right around 422°C, which is 6.4% below the literature value[16]. This test was repeated several times to confirm the decomposition temperature, and every time it was just about 422°C. With this information, and that found in **figure 4** (5% below the literature value), it might be worth checking the instrument's thermometer calibration, as both materials characterized with it reported decomposition temperatures roughly 5% below

where they should be. Regardless, it is close enough to the literature value that it was assumed that the product was still NH$_2$-MIL-53.
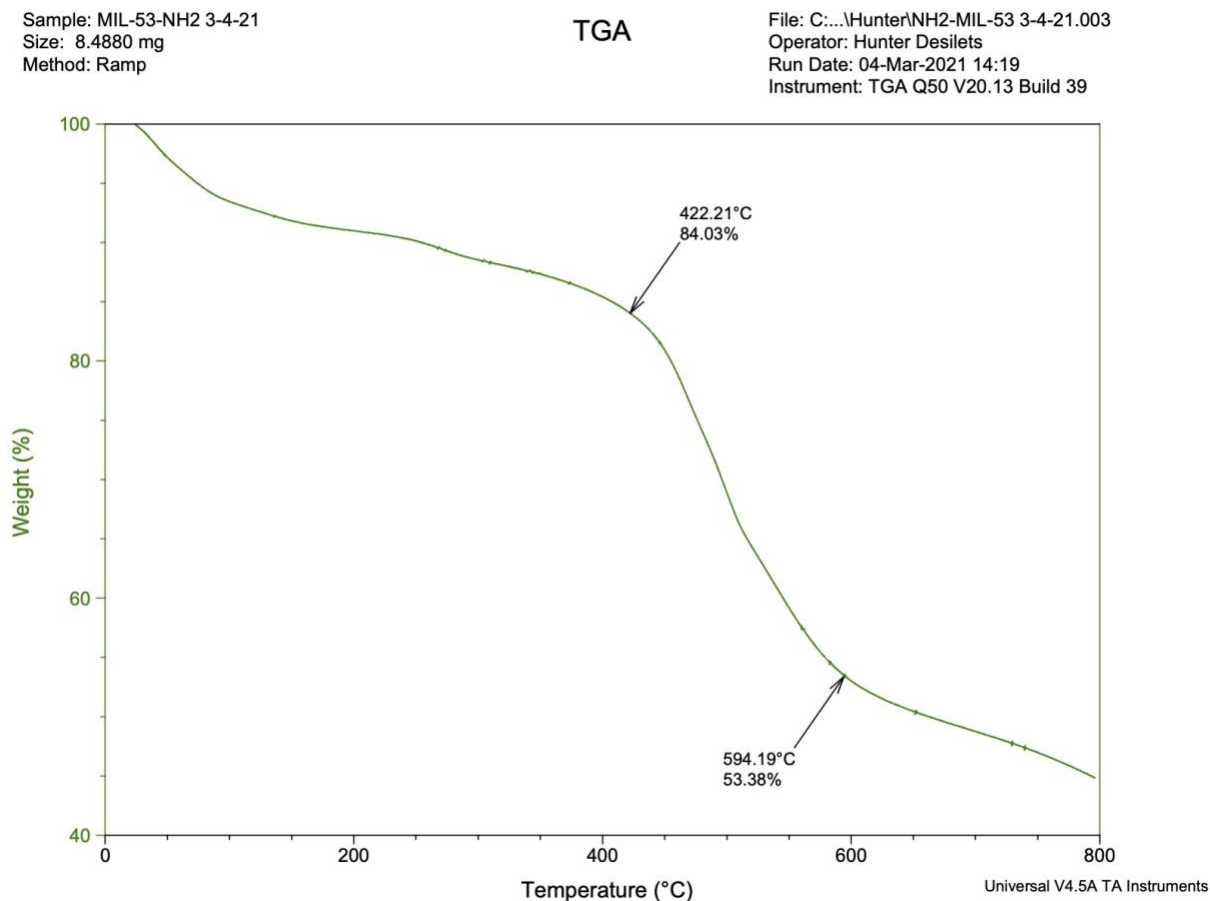
Figure 9: TGA data of suspected NH$_2$-MIL-53. The degradation temperature is similar to the reported literature, being about 6.4% under.

Just like MIL-53, the crystal structure of NH$_2$-MIL-53 has been solved, and it's CIF file published online, which can be seen in **figure 20**. A PXRD of the suspected NH$_2$-MIL-53 was collected and compared to the predicted spectrum, seen in **figure 10**. Clearly seen in the figure, the experimental of NH$_2$-MIL-53 matches up significantly better with its predicted when compared to that of conventional MIL-53. On top of this, the experimental also compares very closely with the PXRD data published in the literature[29]. The discrepancy between the

experimental and theoretical spectra is mainly the pore size of the MOF. The experimental MOF

was made in water, where it can undergo "breathing" effects, changing the size of the pores[17].

The shift in pore size causes the x-ray scattering of the material to shift either up or down,

depending on how the pore changed in size. This is why some peaks have shifted up, and some

have shifted down, as the pore size of the material could have shrunk or expanded[17]. The PXRD

data alone gives clear evidence, but when combined with the data from the IR spectroscopy and

TGA, it clearly confirms that NH_2-MIL-53 can easily be synthesized by using sodium

bicarbonate to first deprotonate the organic linker.
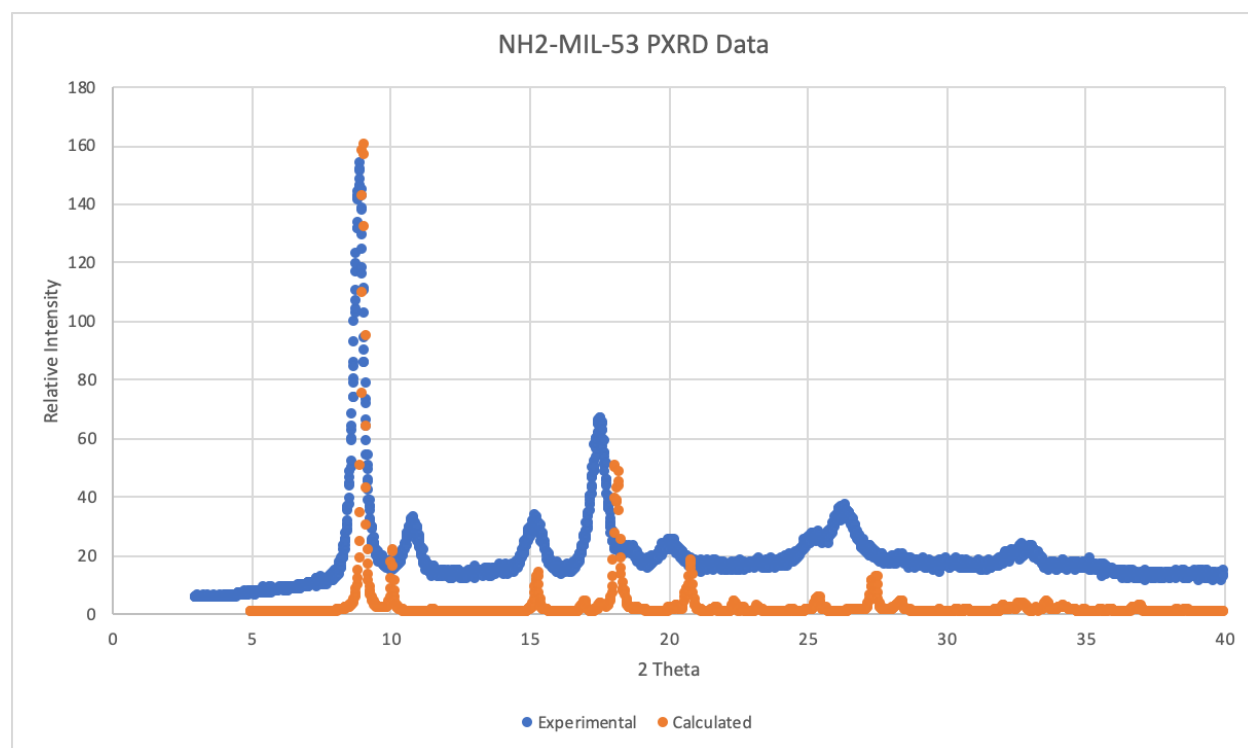
Figure 10: Comparison of experimental and theoretical PXRD values of NH_2-MIL-53. The two

sets of data match significantly better than that of MIL-53.

By using the unit cell of NH_2-MIL-53, the empirical formula of the MOF can be found,

and used to calculate a percent yield. The empirical reaction, as described in **scheme 3**, shows

the molar ratio between aluminum and 2-aminoterephthalate is 1:2. One gram of aluminum

nitrate nonahydrate and 2-aminoterephthalic acid were used to calculate a percent yield of the

reaction. In this calculation, the aluminum ions are just barely the limiting reactant, so the

number of moles of Al^{3+}, 0.002666, corresponds to a theoretical yield of 1.042 g of NH_2-MIL-

53. After combination with the organic linker, filtering, and drying, the mass of product was

0.754 g, which corresponds to a yield of 72.4%. This is a decent yield and could theoretically be

raised by allowing the aluminum and linker solutions more time to react.

$$Al^{3+}_{(aq)} + 2C_6H_4NH_2(CO_2)^{2-}_{2(aq)} + 3.75H_2O_l \rightarrow NH_2 - MIL - 53$$
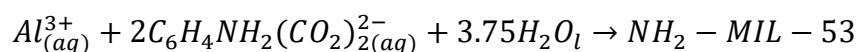
Scheme 3: Empirical reaction of the formation of NH_2-MIL-53

Methylene blue adsorption studies of sodium bicarbonate synthesized NH_2-MIL-53:

Now that it was proven that NH_2-MIL-53 could be synthesized with the use of sodium

bicarbonate as a linker, it was time to try an application of the material. Like mentioned in the

introduction, NH_2-MIL-53 strongly adsorbs to methylene blue in an aqueous environment. The

amount that the dye the material could adsorb to in this research could be quantified by making a

standard curve relating the concentration of MB in solution to its absorption of light at 665 nm.

The standard solutions created can be seen in **figure 17** in the appendix, with the standard curve

being shown in **figure 11**. The goal of any concentration vs. absorbance standard curve is to get

several data points creating a linear relationship with an R^2 to as close as 1 as possible. The R^2 of

figure 11 is 0.9996, meaning the standard curve relating absorbance and concentration is very

accurate and could be used to estimate the concentration of MB in any given solution, given the

absorbance fell in between the bounds of the standardization.
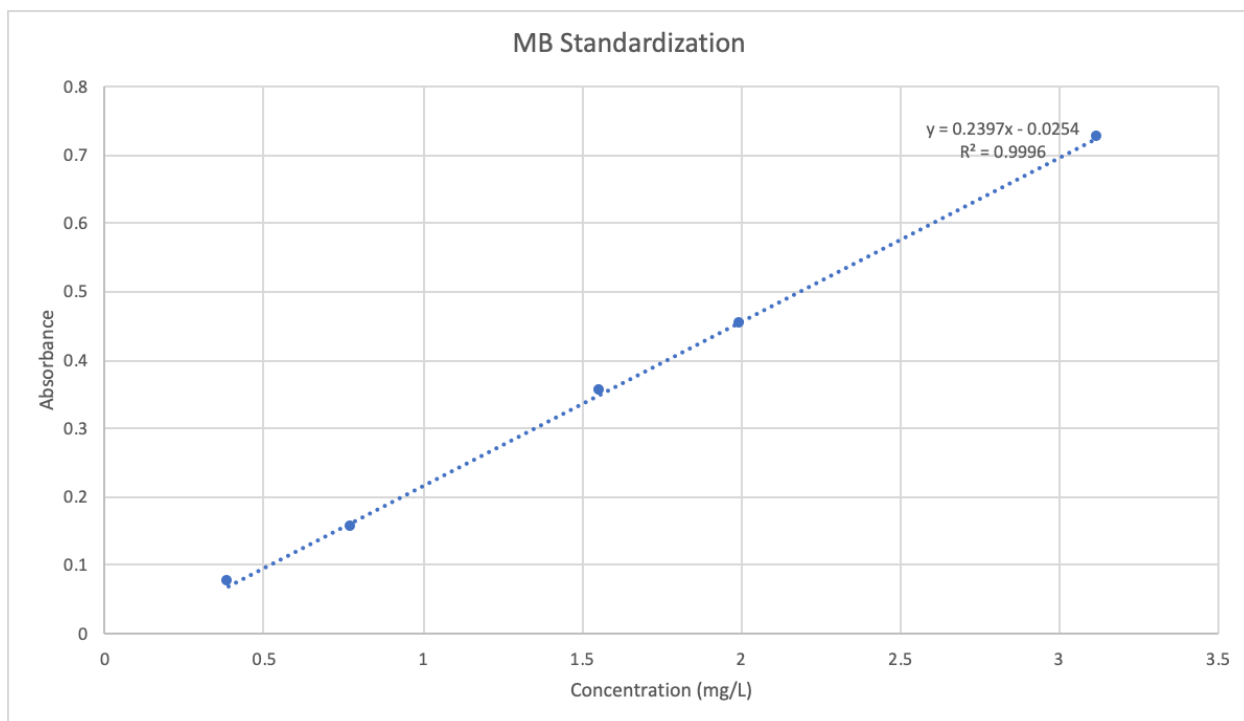
Figure 11: The standardization curve of MB.

Like mentioned in the methods, 10 mg of NH_2-MIL-53 was added to 10 mL of all standard MB solutions created. As the concentrations of each sample were analyzed at the different time intervals, it became clear that the adsorption kinetics follows an exponential decay over time. This assumption was made by analyzing the data from **table 1**, which shows that for the two lowest concentrated MB solutions, the aqueous concentration was cut at least in half. If it followed a 0th order kinetic rate, all of the MB should have been adsorbed after 1 hour, but even after 1 day there was still a little left in solution. For the more concentrated solutions (ie. 12.5, 25, 50 mg/L), they still existed MB in solution after 2 days. It took a week before the most concentrated solution had been reduced to 0, meaning all the MB was trapped on the NH_2-MIL-53.

Standard		30 Min.		1 day:				2 days:			
Conc. (mg/L)	Abs.	Abs.	Conc. (mg/L)	Abs.	Conc. (mg/L)	Percent drop (Abs.)	Quantity Adsorbed (mg/g)	Abs.	Conc. (mg/L)	Percent drop (conc.)	Quantity Adsorbed (mg/g)
50	N/A	N/A	N/A	3.323	N/A	N/A	N/A	1.474	6.03	87.94	43.97
25	3.265	3.318	13.71	0.929	3.76	71.54	21.24	0.092	0.28	98.89	24.72
12.5	2.48	1.999	8.22	0.502	1.99	79.76	10.51	0.026	0.004	99.97	12.50
6.25	1.371	0.981	3.98	0.098	0.30	92.85	5.95	0	0	100	6.25
3.125	0.725	0.52	2.06	0.035	0.04	95.17	3.08	0	0	100	3.13
1.5625	0.354	0.22	0.81	0.027	0.01	92.37	1.55	0	0	100	1.56
0.78125	0.155	0.087	0.26	0.002	0	98.71	0.78	0	0	100	0.78
0.390625	0.073	0.024	0	0.001	0	98.63	0.39	0	0	100	0.39

Table 1: Concentrations of MB in solution at given time intervals.

The interactions that cause the "fast" adsorption of MB on NH_2-MIL-53 is likely the hydrogen bonding taking place. The hydrogen atoms on the amino group of the linker quickly interact with the nitrogen and oxygen atoms on the MB, pulling them in quickly and strongly. Once many of these sites become occupied, it becomes harder for other MB molecules to hydrogen bond, slowing the overall adsorption rate. While this process is happening, the aromatic rings of the linker and MB are also interacting via π-π stacking – an effect caused by the overlap of the π-orbitals in the molecules. This interaction is much weaker and slower than

hydrogen bonding, but still occurs nonetheless, and is the primary driver continuing adsorption of MB when all hydrogen bonding sites are filled.

The most concentrated MB-NH$_2$-MIL-53 material (50 mg/L), was taken out of the cleaned water and dried. All of the spectroscopic techniques used for the characterization of the MOFs by themselves were used on this material to see if the dye could be observed, but unfortunately only the PXRD data looks different from the dye-free counterpart, which can be seen in **figure 18** in the appendix, with the IR spectra of the material in **figure 19**. This is likely due to the fact that amount of MB present was so minute compared to the NH$_2$-MIL-53. At the most concentrated, 10 mL of a 50 mg/L solution was adsorbed onto 10 mg of NH$_2$-MIL-53. That means only 0.5 mg of MB were adsorbed onto the material, which was apparently not enough for the instruments to see it present. However, no fancy instrumentation needs to prove that the MB was in fact bound to the NH$_2$-MIL-53, because eyes alone were able to make that assumption. MB very easily stains the solution it is in a deep blue color. NH$_2$-MIL-53 is a yellow color, and as it begins to adsorb MB it shifts from yellow, to green, to teal, to blue. At the same time the solution begins to become less blue, it is rid of any color whatsoever. This can be clearly seen in **figure 12**, which shows the gradual color shift of the NH$_2$-MIL-53 material as more dye is adsorbed.

Figure 12: As NH$_2$-MIL-53 adsorbs more MB, it progressively becomes bluer. The flasks on the left were the least concentrated MB solutions, while the flasks on the right were the most concentrated.

The last experiment was to calculate the desorption of MB from NH$_2$-MIL-53. To prepare this, a solution of 100 mg/L MB was prepared with 10 mg of NH$_2$-MIL-53. The MOF was unable to adsorbed all of the dye, and analysis of the solution using **figure 11** showed the material had adsorbed 90 mg/L. Removing the dye from the MOF has been done conventionally by flushing the dye-saturated material with a solvent solution consisting of 40% methanol and 60% acetonitrile. The material was placed on top of some glass wool on the inside of a glass pipet, but when flushed with 25 mL of the flushing solution, only 8 mg/L was taken out. This was found by roto-evaporating the solvent solution to remove it all, with the remaining MB being dissolved in 10 mL of deionized water and analyzed using UV-vis spectroscopy and **figure 11**. To try and remove more dye, the entire 10 mg of material was placed in a 50 mL beaker with 40 mL of the solution on top. Every day for a week the supernatant was removed with clean solution replacing it, but this was only able to remove an additional 13 mg/L MB. It is unknown why the green-synthesized NH$_2$-MIL-53 held on to the dye so much stronger than the literature materials[16], but some theories can be made. The MOF was created almost instantly when the aluminum and linker solutions were combined, preventing large crystals from forming. This could have increased the surface area of the MOF in comparison to the conventional solvothermal synthesis route, increasing the total hydrogen bonding sites available. These bonds are much stronger than the π-π stacking, and might not be able to be broken by the standard flushing solution. However, this issue was not investigated any further, as time in the lab began getting low.

Conclusions / Future Work

For the first time, this research proved that two metal-organic frameworks, MIL-53 and NH$_2$-MIL-53 could be synthesized by deprotonation of the organic linker molecules (terephthalic acid, and 2-aminoterephthalic acid, respectively) using sodium bicarbonate, and subsequent reaction with an Al^{3+} solution. This method is "greener" than the previously reported "green" synthesis of MIL-53 as it removes the need of sodium hydroxide, a highly corrosive and toxic base. By simply calculating the mass of aluminum nitrate and 2-aminoterepthalic acid needed to be in a 1:2 molar ratio, the MOF can be made with hypothetically no waste, as besides the sodium bicarbonate, all of the excess starting material can be recovered. This MOF has been proven to be highly selective towards some emerging organic contaminants, including methylene blue and malachite green – two toxic cationic dyes. If a wastewater solution is found to be contaminated with MB, this synthesis strategy can be followed to quickly prepare an adsorbent material capable of cleaning the dye out of the water, while using relatively green techniques.

Future works include the analysis of a solution treated with the green-synthesized NH$_2$-MIL-53 for fragments of either aluminum or 2-aminoterephalate. It is unknown whether the material holds up through multiple uses, or if it deteriorates slowly in solution. Further investigation into why the green-synthesized material held so strongly onto MB once it was adsorbed in comparison to previous works. Also, now that this work has shown sodium bicarbonate can be used to create MOFs, a library of MOFs able to be synthesized via the methods provided in this work should be created.

Acknowledgements

**References**

1. General Assembly resolution 64/292, *The human right to water and sanitation,* A/RES/64/292 (28 July **2010**), available from http://undocs.org/en/A/RES/64/292.
2. Prüss-Üstün, A.; Bos, R.; Gore, F.; Bartram, J.; World Health Organization. *Safe Water, Better Health: Costs, Benefits and Sustainability of Interventions to Protect and Promote Health*; **2008**.
3. Roller, Z.; US Water Alliance. *Closing the Water Access Gap in the United States;* **2019**. Available from http://uswateralliance.org/sites/uswateralliance.org/files/publications/Closing%20the%20Water%20Access%20Gap%20in%20the%20United%20States_DIGITAL.pdf
4. Overpeck, J. T.; Udall, B. Climate Change and the Aridification of North America. *Proc. Natl. Acad. Sci.* **2020**, *117* (22), 11856–11858. https://doi.org/10.1073/pnas.2006323117.
5. Current Map. (**2021**, April 26). Retrieved December 09, 2020, from https://droughtmonitor.unl.edu/
6. Megafarms and deeper wells are draining the water beneath rural Arizona – quietly, irreversibly https://www.azcentral.com/in-depth/news/local/arizona-environment/2019/12/05/unregulated-pumping-arizona-groundwater-dry-wells/2425078001/ (accessed Apr 28, 2021).
7. Völker, J.; Stapf, M.; Miehe, U.; Wagner, M. Systematic Review of Toxicity Removal by Advanced Wastewater Treatment Technologies via Ozonation and Activated Carbon. *Environ. Sci. Technol.* **2019**, *53* (13), 7215–7233. https://doi.org/10.1021/acs.est.9b00570.
8. Water Treatment | Public Water Systems | Drinking Water | Healthy Water | CDC https://www.cdc.gov/healthywater/drinking/public/water_treatment.html (accessed Dec 18, 2020).
9. Brillas, E.; Martínez-Huitle, C. A. Decontamination of Wastewaters Containing Synthetic Organic Dyes by Electrochemical Methods. An Updated Review. *Appl. Catal. B Environ.* **2015**, *166–167*, 603–643. https://doi.org/10.1016/j.apcatb.2014.11.016.
10. External Medicine: Discarded Drugs May Contaminate 40 Million Americans' Drinking Water https://www.scientificamerican.com/article/pharmaceuticals-in-the-water/ (accessed Dec 18, 2020).
11. Zhou, H.-C.; Long, J. R.; Yaghi, O. M. Introduction to Metal–Organic Frameworks. *Chem. Rev.* **2012**, *112* (2), 673–674. https://doi.org/10.1021/cr300014x.
12. Feng, L.; Wang, K.-Y.; Willman, J.; Zhou, H.-C. Hierarchy in Metal–Organic Frameworks. *ACS Cent. Sci.* **2020**, *6* (3), 359–367. https://doi.org/10.1021/acscentsci.0c00158.

13. Ma, X.; Chai, Y.; Li, P.; Wang, B. Metal–Organic Framework Films and Their Potential Applications in Environmental Pollution Control. *Acc. Chem. Res.* **2019**, *52* (5), 1461–1470. https://doi.org/10.1021/acs.accounts.9b00113.

14. Brillas, E.; Martínez-Huitle, C. A. Decontamination of Wastewaters Containing Synthetic Organic Dyes by Electrochemical Methods. An Updated Review. *Appl. Catal. B Environ.* **2015**, *166–167*, 603–643. https://doi.org/10.1016/j.apcatb.2014.11.016.

15. Cheng, J.; Zhan, C.; Wu, J.; Cui, Z.; Si, J.; Wang, Q.; Peng, X.; Turng, L.-S. Highly Efficient Removal of Methylene Blue Dye from an Aqueous Solution Using Cellulose Acetate Nanofibrous Membranes Modified by Polydopamine. *ACS Omega* **2020**, *5* (10), 5389–5400. https://doi.org/10.1021/acsomega.9b04425.

16. Li, C.; Xiong, Z.; Zhang, J.; Wu, C. The Strengthening Role of the Amino Group in Metal–Organic Framework MIL-53 (Al) for Methylene Blue and Malachite Green Dye Adsorption. *J. Chem. Eng. Data* **2015**, *60* (11), 3414–3422. https://doi.org/10.1021/acs.jced.5b00692.

17. Loiseau, T.; Serre, C.; Huguenard, C.; Fink, G.; Taulelle, F.; Henry, M.; Bataille, T.; Férey, G. A Rationale for the Large Breathing of the Porous Aluminum Terephthalate (MIL-53) upon Hydration. *Chem. Weinh. Bergstr. Ger.* **2004**, *10* (6), 1373–1382. https://doi.org/10.1002/chem.200305413.

18. Huang, L.; Cai, J.; He, M.; Chen, B.; Hu, B. Room-Temperature Synthesis of Magnetic Metal–Organic Frameworks Composites in Water for Efficient Removal of Methylene Blue and As(V). *Ind. Eng. Chem. Res.* **2018**, *57* (18), 6201–6209.

19. Green Chemistry: Principles and Practice - Chemical Society Reviews (RSC Publishing) https://pubs.rsc.org/en/content/articlelanding/2010/cs/b918763b#!divAbstract (accessed Dec 18, 2020).

20. Yang, Q.; Sheng, M.; Huang, Y. Potential Safety Hazards Associated with Using *N* , *N* -Dimethylformamide in Chemical Reactions. *Org. Process Res. Dev.* **2020**, *24* (9), 1586–1601. https://doi.org/10.1021/acs.oprd.0c00330.

21. Sánchez-Sánchez, M.; Getachew, N.; Díaz, K.; Díaz-García, M.; Chebude, Y.; Díaz, I. Synthesis of Metal–Organic Frameworks in Water at Room Temperature: Salts as Linker Sources. *Green Chem.* **2015**, *17* (3), 1500–1509. https://doi.org/10.1039/C4GC01861C.

22. Baking Soda: Exploring the Science of Baking Soda. *ACS Axial*, 2018.

23. I., M.; Saleh, H. A. M.; Qasem, K. M. A.; Shahid, M.; Mehtab, M.; Ahmad, M. Efficient and Selective Adsorption and Separation of Methylene Blue (MB) from Mixture of Dyes in Aqueous Environment Employing a Cu(II) Based Metal Organic Framework. *Inorganica Chim. Acta* **2020**, *511*, 119787. https://doi.org/10.1016/j.ica.2020.119787.

24. Shi, L.; Hu, L.; Zheng, J.; Zhang, M.; Xu, J. Adsorptive Removal of Methylene Blue from Aqueous Solution Using a Ni-Metal Organic Framework Material. *J. Dispers. Sci. Technol.* **2016**, *37* (8), 1226–1231. https://doi.org/10.1080/01932691.2015.1050731.

25. Radnai, T.; May, P.; Hefter, G.; Sipos, P. Structure of Aqueous Sodium Aluminate Solutions: A Solution X-ray Diffraction Study. *J. Phys. Chem.* **1998**, 102, 7841-7850.

26. 21.3: Spectroscopy of Carboxylic Acids https://chem.libretexts.org/Bookshelves/Organic_Chemistry/Map%3A_Organic_Chemistry_(Wade)/21%3A_Carboxylic_Acids/21.03%3A_Spectroscopy_of_Carboxylic_Acids (accessed May 2, 2021).

27. Little, E. J.; Jones, M. M. A Complete Table of Electronegativities. *J. Chem. Educ.* **1960**, *37* (5), 231. https://doi.org/10.1021/ed037p231.

28. Andonova, S.; Ivanova, E.; Yang, J.; Hadjiivanov, K. Adsorption Forms of CO$_2$ on MIL-53(Al) and MIL-53(Al)–OH$_x$ As Revealed by FTIR Spectroscopy. *J. Phys. Chem. C* **2017**, *121* (34), 18665–18673. https://doi.org/10.1021/acs.jpcc.7b05538.

29. Cheng, X.; Zhang, A.; Hou, K.; Liu, M.; Wang, Y.; Song, C.; Zhang, G.; Guo, X. Size- and morphology-controlled NH2-MIL-53(Al) prepared in DMF−water mixed solvents. *Dalton Trans*. **2013**. ,42,13698−13705.

Appendix:
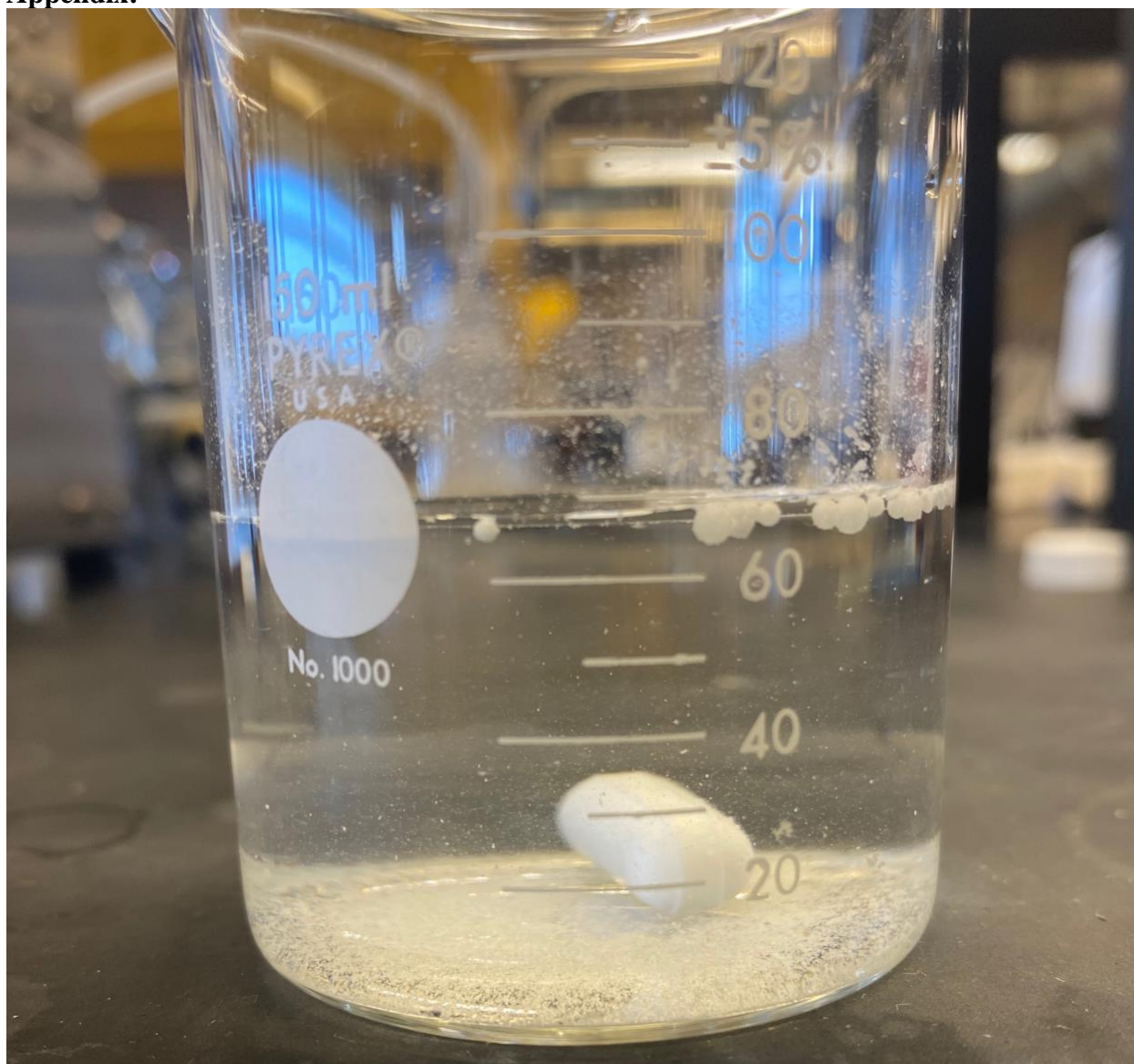
Figure 13: Incomplete dissociation of terephthalic acid.
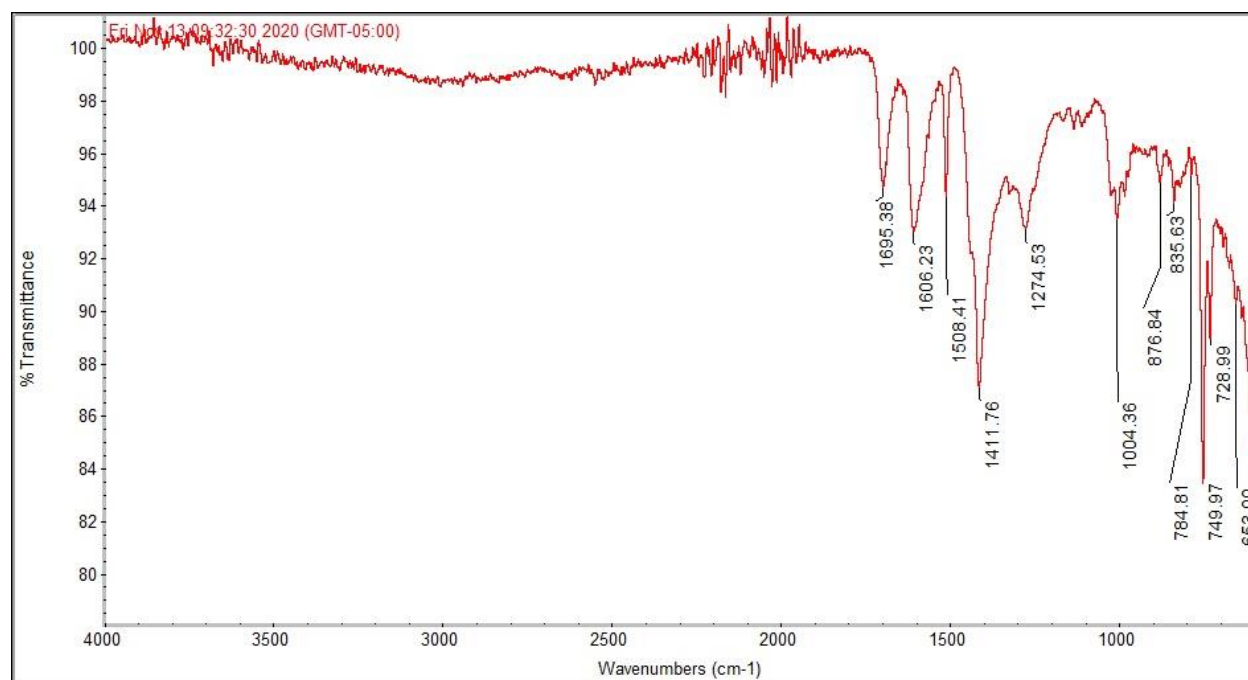
Figure 14: IR spectrum of MIL-53 via bicarbonate. This spectrum is remarkably similar to the one found in **figure 3**, giving good evidence that bicarbonate can be used in the synthesis of MIL-53 instead of the harsher hydroxide.
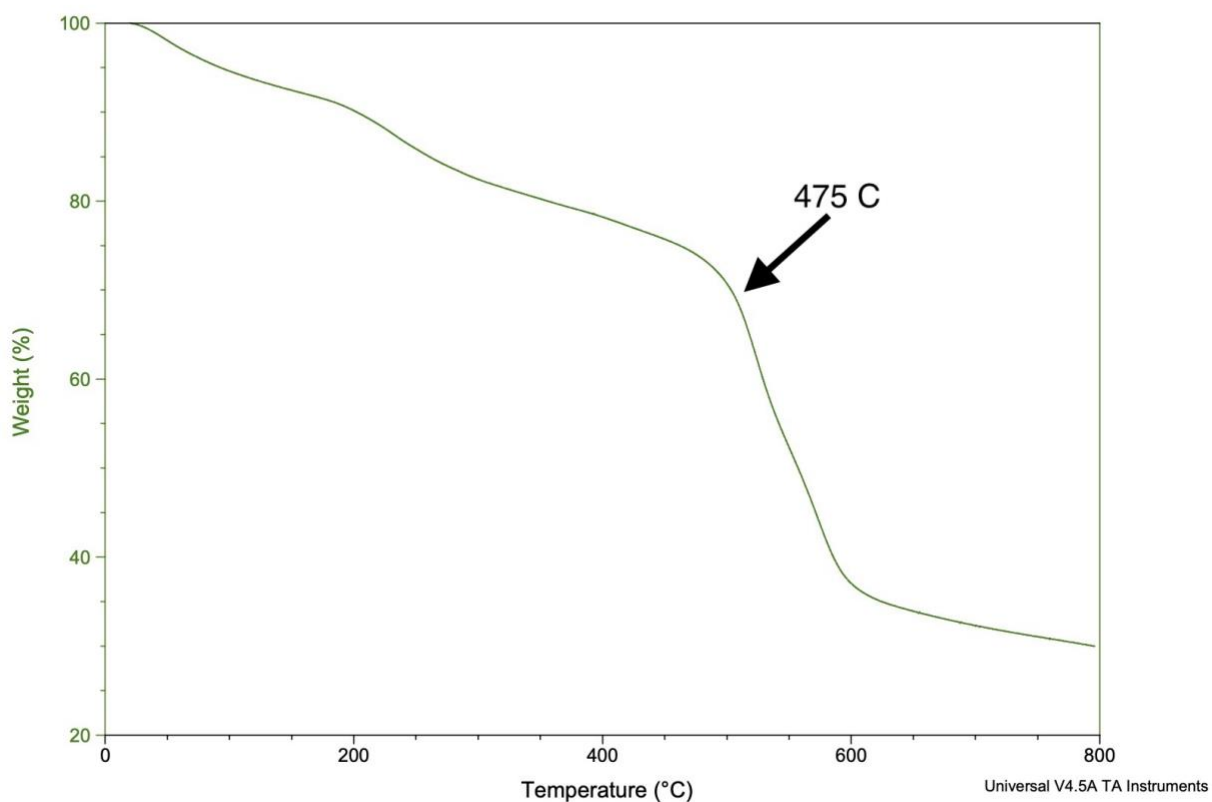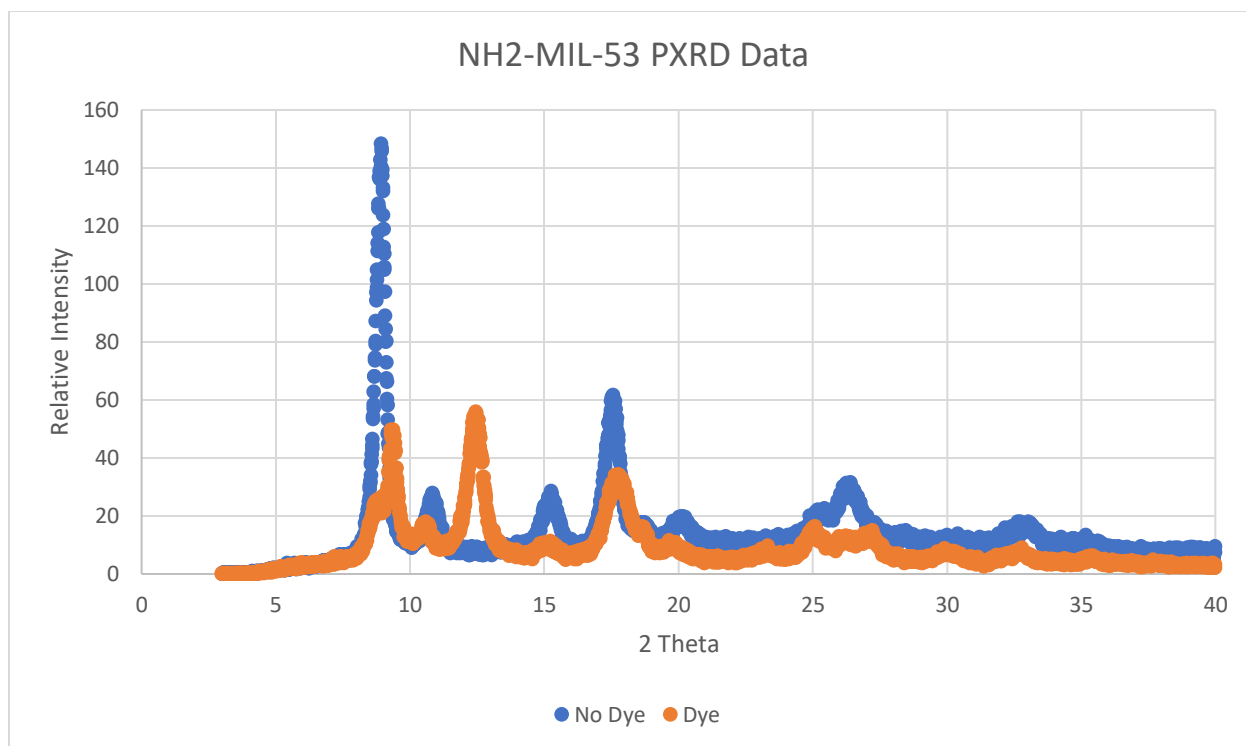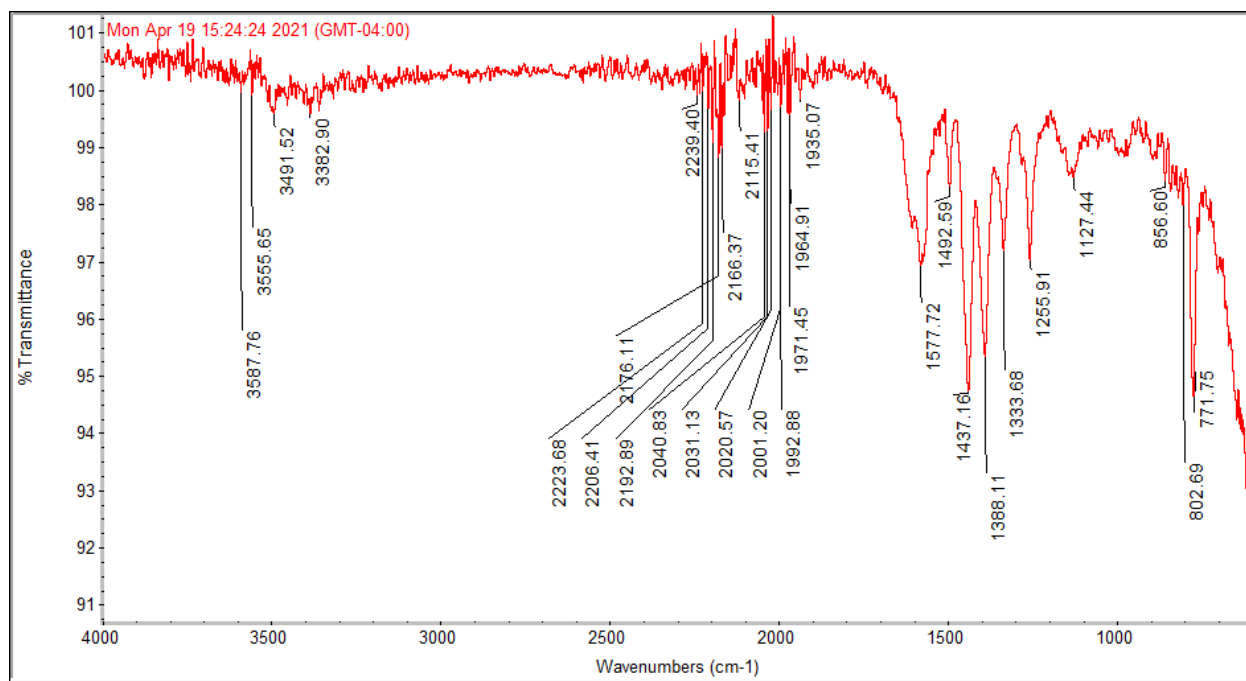
Figure 15: TGA of MIL-53 via bicarbonate
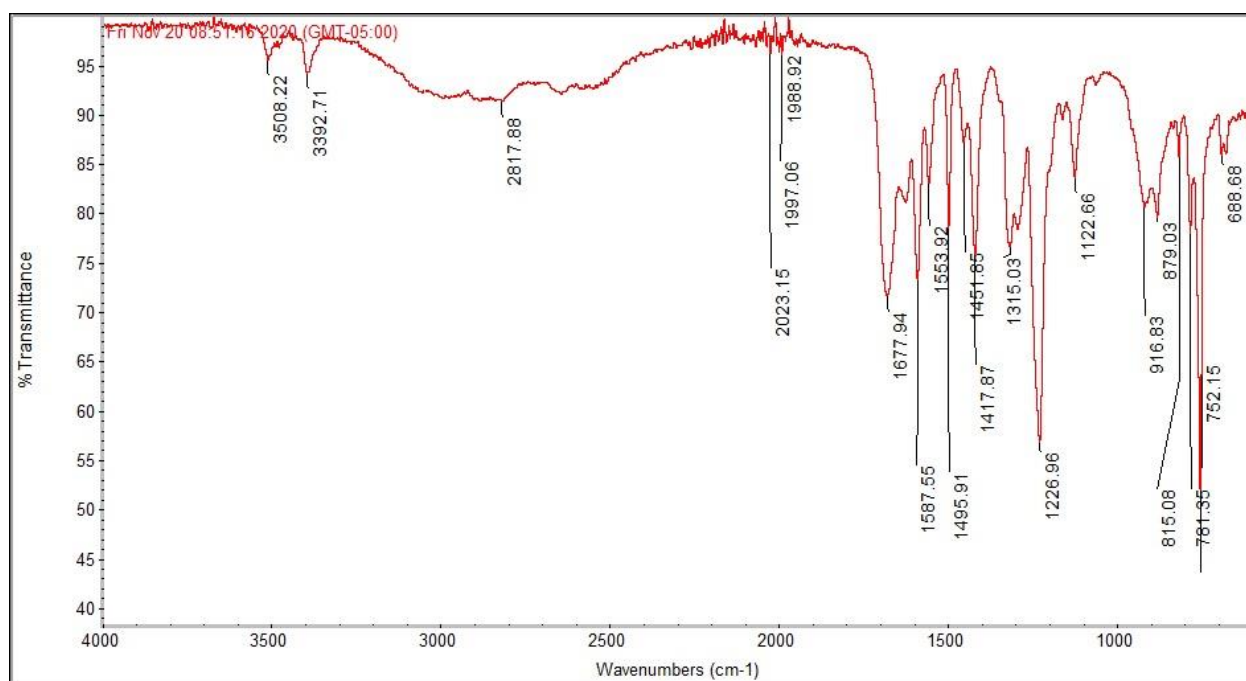
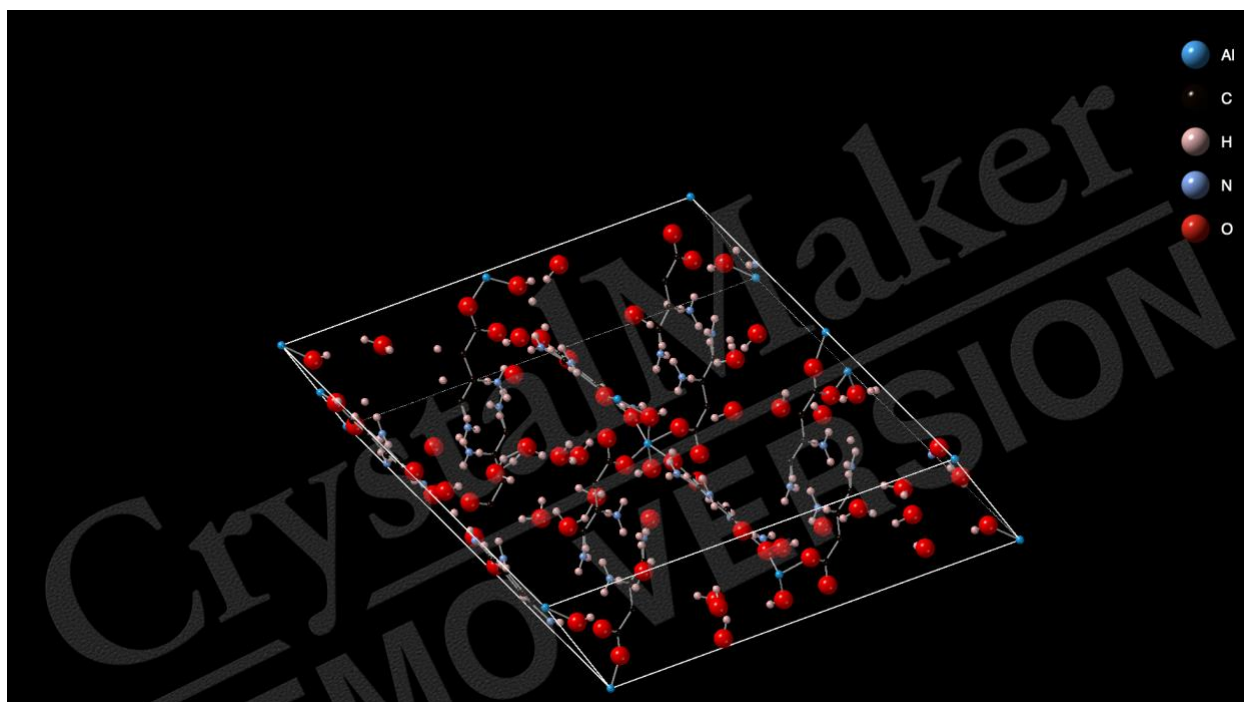**Figure 16:** IR spectrum of 2-aminoterephthalic acid

Figure 17: Standard solutions of MB ranging from 50 mg/L to 0.39 mg/L, cut in half every time.

Figure 18: Comparison of the PXRD data for dye-free and dye-saturated NH2-MIL-53

Figure 19: IR spectrum of the MB-saturated NH$_2$-MIL-53

Figure 20: Crystal Structure of NH$_2$-MIL-53