

Canh Le, Tu Nguyen

ZIF 67 AS PHOTOCATALYST FOR DYE DESTRUCTION

Thesis

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ABSTRACT

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| Centria University of Applied Sciences | Date March 2019 | Author Canh Le Tu Nguyen |
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| Instructor Laura Rahikka | Pages 41 | |
| Supervisor Laura Rahikka | | |
| <p>Environmental Protection has been globally recognized as the essential issues as well as remarkable debates of every countries in the worlds. One of those problems is the water pollution which cause the devastation of any aquatic creatures and human activities. There is a massive source which contribute to the contamination of water but specifically the dyes and pigments from textile industry generates an enormous hazardous chemical directly to the water environment. Therefore, a method, especially photocatalysis is optimal for the destruction of dye color before discharging.</p> <p>Additionally, the selection of catalyst is also important for the efficiency of the photocatalytic process. Zeolitic imidazolate framework 67 (ZIF-67) is the chosen substance for the laboratory experiment. ZIF 67 is one class of metal organic frameworks (MOFs) which structured by the connection of group of organic linkers and metal ions. With the special properties such as porosity and chemical stabilities, this compound can be applied in many aspects in industry such as sorption, sensing function, medicine and so on.</p> <p>The main purpose of the final thesis might be divided into two parts. Initially, searching and gathering the necessary information of photocatalysis, metal organic frameworks, zeolitic imidazolate frameworks (ZIFs) and the mechanism of free radicals in order to release a fundamental background of their properties and production. The next part is experimental performance provides the manufacture of ZIF 67, the influence of its chemical to the destruction of dye (congo red) as well as the determination of free radicals through the reaction.</p> | | |

Key words

Metal Organic Frameworks, Zeolitic Imidazolate Frameworks, Photocatalysis and Free Radicals

ABSTRACT

CONCEPT DEFINITIONS

CONTENTS

| | |
|--|-----------|
| 1 INTRODUCTION..... | 1 |
| 2 METAL ORGANIC FRAMEWORKS (MOFs) | 3 |
| 3 METAL ORGANIC FRAMEWORKS NETWORKS | 7 |
| 3.1 3D Net Works | 7 |
| 3.2 Unitary and Binary nets | 8 |
| 3.3 Ternary Nets | 10 |
| 4 SYNTHESIS OF MOFs..... | 11 |
| 5 APPLICATIONS | 13 |
| 5.1 Sorption Applications | 13 |
| 5.2 MOFs as Catalysts..... | 14 |
| 5.2.1 Framework activity | 14 |
| 5.2.2 Encapsulation of active species | 14 |
| 5.3 MOFs Application for Medicine | 15 |
| 5.4 The Luminescence properties of MOFs | 15 |
| 5.5 Sensing Applications of MOFs | 15 |
| 6 ZEOLITIC IMIDAZOLATE FRAMEWORKS (ZIFs)..... | 16 |
| 7 SYNTHESIS OF ZIFs | 18 |
| 7.1 Synthesis of Power ZIFs | 18 |
| 7.1.1 Solvent – based synthesis | 19 |
| 7.1.2 Non-solvent synthesis | 20 |
| 7.2 Synthesis of Film/Membrane ZIFs | 21 |
| 7.2.1 Pure ZIF films and membranes | 22 |
| 7.2.1.1 Secondary growth crystallization | 22 |
| 7.2.1.2 In situ crystallization..... | 23 |
| 7.2.2 Synthesis of ZIF based film/membrane composites | 25 |
| 8 PHOTOCATALYSIS | 26 |
| 8.1 Photocatalytic mechanism | 27 |
| 8.2 Factors Affecting to The Photocatalysis..... | 29 |
| 8.2.1 Crystal structure, shape, size and surface area of catalyst | 29 |
| 8.2.2 The effect of temperature | 29 |
| 8.2.3 The effect of pH level | 29 |
| 8.2.4 The effect of light intensity | 30 |
| 8.2.5 The effect of catalyst’s amount | 30 |
| 8.2.6 The effect of contaminants’ concentration in wastewater | 30 |
| 8.3 The pros and cons of Photocatalysis..... | 31 |

| | |
|---|-----------|
| 9 FREE RADICALS | 32 |
| 9.1 Reaction Mechanism of Free radicals | 32 |
| 9.2 The production of Free Radicals | 34 |
| 10 EXPERIMENT EXECUTION | 35 |
| 10.1 Preparation..... | 35 |
| 10.2 Procedure..... | 36 |
| 10.2.1 The fabrication of ZIF 67 as well as its function as photocatalyst in dye..... | 36 |
| 10.2.2 Determination of hydroxyl radicals | 36 |
| 10.2.3 Determination of radicals with the participation of Potassium Iodate (KI), Iso Propanone (IPA) and Benzoquinone (BQ). | 37 |
| 10.3 Data recorded..... | 37 |
| 10.4 Evaluation of the experiments | 41 |
| 11 CONCLUSIONS | 42 |
| REFERENCES..... | 43 |

FIGURES

| | |
|--|----|
| FIGURE 1.The development of Coordination Polymers from 1990 until 2006..... | 3 |
| FIGURE 2.The molecule shapes of Metal Organic Frameworks | 4 |
| FIGURE 3.Design Principle of Metal Organic Framework | 5 |
| FIGURE 4.The 3D networks of MOFs..... | 8 |
| FIGURE 5.Binary nets examples of Different MOFs..... | 9 |
| FIGURE 6.Ternary nets examples of Different MOFs..... | 10 |
| FIGURE 7.4'-4- bipyridine with different structures..... | 11 |
| FIGURE 8.Structure of Different Zeolitic Imidazolate Frameworks | 17 |
| FIGURE 9.The schematic graph of ZIFs' synthesis | 18 |
| FIGURE 10.The mechanochemical synthesis of ZIFs..... | 21 |
| FIGURE 11.ZIF 8 membrane formation by reactive seeding..... | 23 |
| FIGURE 12.The solvent evaporation method..... | 24 |
| FIGURE 13.The MMMs' synthesis process..... | 25 |
| FIGURE 14.Photocatalysis Mechanism | 27 |
| FIGURE 15.The oxidation and reduction process | 28 |
| FIGURE 16.The reaction of organic compounds and free radicals..... | 32 |
| FIGURE 17.The reaction between two free radicals | 33 |
| FIGURE 18.The arrangement of organic compounds with catalyst..... | 33 |
| FIGURE 19a.Thermal generation reaction | 34 |
| FIGURE 19b.Photochemical generation reaction..... | 34 |
| FIGURE 19c.Redox generation reaction | 34 |
| FIGURE 20.ZIF 67 product..... | 35 |
| FIGURE 21.The measurement of absorption level..... | 35 |
| FIGURE 22.2-hydroxyterephthalic acid under the light with 315nm and compared to water..... | 36 |
| FIGURE 23.Fluorescence spectral changes observed during illumination of ZIF 67 in 4×10^{-4} M NaOH solution of terephthalic acid (excitation at 315 nm). | 37 |
| FIGURE 24. Congo red removal rates via ZIF 67 photocatalysis in the presence of KI (hole scavenger), isopropanol (hydroxyl radical scavenger), and benzoquinone (superoxide scavenger) | 38 |
| FIGURE 25.The color's change of Congo red. | 39 |

1 INTRODUCTION

It is not doubt that water has been recognized as the necessary element which affect the any life on earth. Annually, there are prediction that more than 3.2 million people died because of the lack of water quality such as polluted water, ineffective supervisor as well as poor wastewater treatment system. There are many reasons for the contamination sources of water which are industrial area and human daily routine, agricultural activities and the natural pollution. Among them, the industrial area remarkably takes a huge responsibility for the water pollution. Water pollution means that the hazardous impurities such as pesticides, herbicides, textile dyes, resins and so on. There are more than 0.7 millions tons of organic dyes produced each year which applied in many demands such as fashion, cosmetics, painting, foods, plastic and so on. Dyes from the textile industry has been detected as the most polluting factor comparing to the others in industrial areas. This issue occupies 25% of toxic chemicals to water system by dye discharge. There are approximate 10000 various dyes utilized in industry and 50% of those is azo dyes which chemically are soluble organic colored compounds. The reasons why dyes should be removed from water because dye is high total dissolved solids in the wastewater also there are many heavy metals appeared in the dye such as Cr, Cu, As and Cd. Moreover, the dyes also contain free chlorine in the structure that lead to the stability of dye texture so it is really difficult to destroy.

There a lot of method suggested and tested for the elimination of dye color in wastewater which is classified as physical, chemical and biological approaches. Among them, the conventional biological solution has been mentioned as ineffective because of the high salinity of wastewater containing dyes also the recalcitrant feature of dyes. Besides, the chlorination and ozonation method need high cost for the operation process. There are also a lot of method such as adsorption of activated carbon, reverse osmosis, ultrafiltration, ion exchange using chemicals have been applied but they also consequence the secondary pollution leading to the further treatment method. Nowadays, photocatalysis has been considered as the successful method for the destruction of dye color following many factors:

- The flexibility of treatment.
- Totally removal of pollutants
- Chemicals can be recycled after the treatment process
- It is cost-affordable and eco-frendly

The main purpose of the thesis is the research of ZIF especially ZIF 67 for the photocatalytic method which consists of the fundamental definition, reaction mechanism as well as noticeable parameters and factors influencing on the process. ZIF 67 contain two metals Co and Zn which are transition metals so

the areas of band gap energy are huge. During the wastewater treatment process, the metals can widen the absorbance to ultraviolet light to obtain the successful photocatalytic activity. Moreover, Zn contain in ZIF can create the photogenerated electrons that lead to the hole move in the opposite direction of electron and cause charge separation.

2 METAL ORGANIC FRAMEWORKS (MOFs)

Metal- Organic Frameworks (MOFs) or porous coordination polymers (PCPs) is defined as a new type of porous solids was found over 50 years ago. In 1964, the coordination polymers' area was officially published and researched. The first of study about coordination polymers based on Fe-CN-Fe linkages and chemicals has the similar structures. However, the achievement of metal organic framework aspect was begun until 1980 by Robson who created "node-and-spacer" method by the combination of transition metal ions and organic ligands in order to generate a linking network. In 1990s, these materials take the important consideration by the chemist Omar Yaghi and his partners. His team worked on the synthesis the coordination networks between metal cations and organic ligands. After that, the neutral MOFs were synthesized through the replacement of organic ligands by 4,4'- bipyridine moieties. (Wang 2006, 13-14; Raghavan et al. 2014, 65)

Figure 1 illustrates the metal organic frameworks's milestone for more than 25 years.

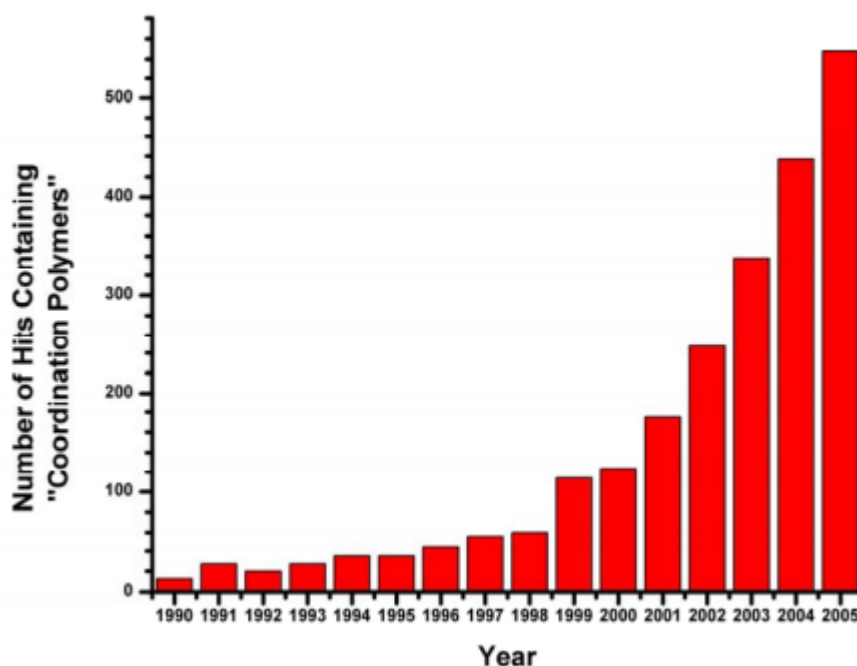


FIGURE 1. The development of Coordination Polymers from 1990 until 2006 (Wang 2006, 14)

Their typical properties are the porosity which allows guest molecules diffusing into bulk structure. Besides, the shape and size selectivity of the guests are adjusted by their pores when cooperation together. Yaghi et al has detected the MOFs porous structure created from connection of between metal ions and organic linkers or bridging ligands by coordinative bonding. Because of the MOFs' tunable

nano-porosity, this material is harder than others such as zeolites and other metal oxides. In addition, the oxygen atoms can be replaced by rigid organic ligands or linkers that connects the inorganic or ion clusters so that creating one, two and three -dimensional frameworks and MOFs is also classified as organic compounds. According to Robson's method, the structure connection of the organic based linear spacers and the metal- based nodes in order for the formation of different shapes which could be square, tetrahedral, octahedral and so on. Besides, nodes or spacers could be the function of not only metal centers but also organic ligands. (Wang 2006, 14-15)

Figure 2 demonstrate the examples of different dimensional shapes.

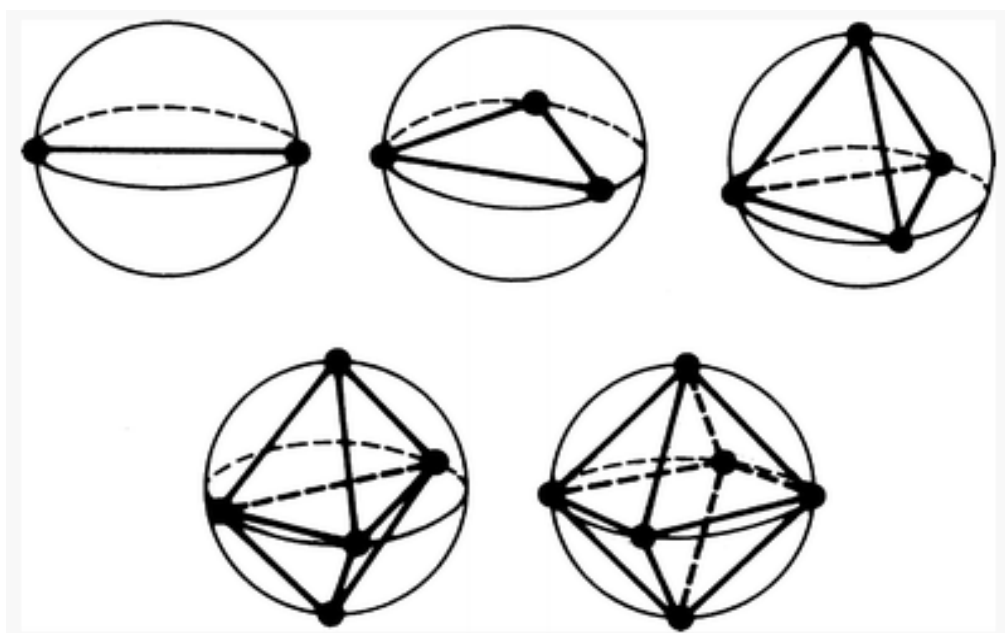


FIGURE 2. The molecule shapes of Metal Organic Frameworks (Gillespie 2009)

The illustration of MOFs can be exemplified as crystal which can be designed the new supramolecular materials because there are at least two components in MOFs' structure, so they can be capable of self-combination. There are two various principles applied popularly for the design of MOFs. The first method based of Robson's strategy" node-and-spacer" which blocks of building represent the topological points whereas lines and nets are the symbol of combinations. Meanwhile, Wells created a new system regrading to the basis of crystal chemistry which is the method concentrating on the realm of metal-organic compounds and coordination polymers. (Wang 2006, 15)

The general formation of MOFs is described in figure 3

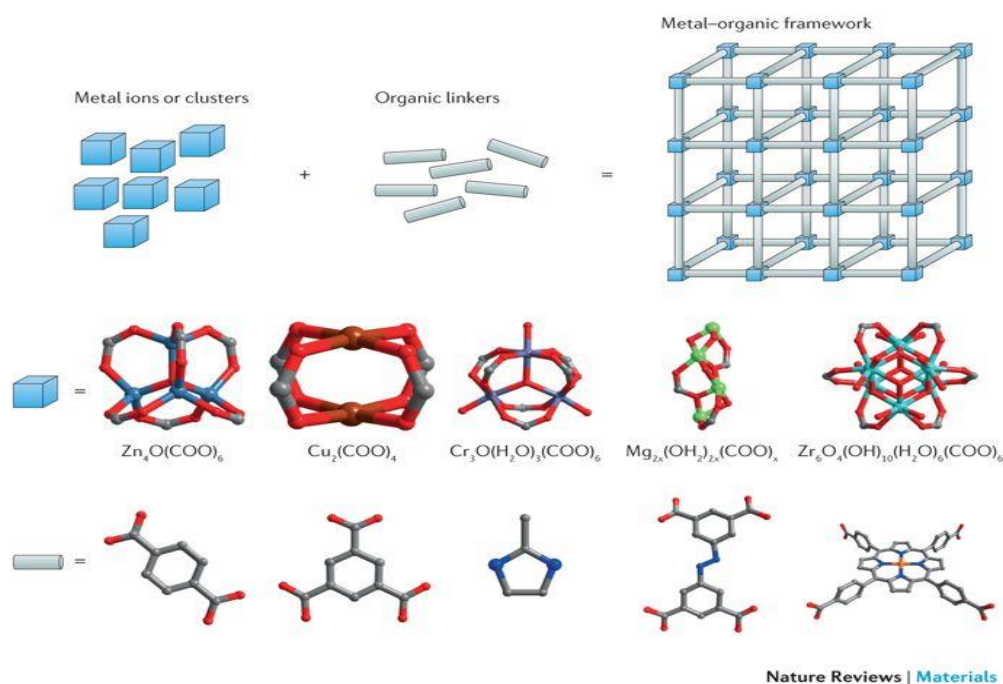


FIGURE 3. Design Principle of Metal Organic Framework (Howart et al. 2016)

The method for demonstration of Metal-Organic's texture is based on the Well's rules. This approach describes a symbol (n, p) in which n is represented as the number of polygons' edges in the net while p is stood for the vertices' connectedness. However, due to the obvious over-simplification of this method, so it can not be represented for several different 3D structure. Therefore, O' Keeffe designed a new method named Schläfli symbols or can be recognized as vertex symbols. In O' Keeffe symbols, the structure is introduced as $A_a \cdot B_b \cdot [\dots] \cdot M_m$ where the ring size of the network is symbolized as the letter A, B, ..., M while the angles which created by the meeting position of rings in the network is symbol of a, b, ... m. (Wang 2006, 18)

There are four compulsory regulations that need to be complied when using Schläfli symbols to demonstrate the MOFs' network which are displayed below:

- The vertex symbols' principle can be applied for every nets' types and the number of angles for a m -connected node is given by the formula: $m \cdot (m-1) / 2$.
- The long vertex symbol is simplified by the short chain positioned in each angle. For example, with MOF network contain two (5,2) nets is written as 5^2 .
- The next rule is that the MOFs' structure contains opposite angles with smallest rings are written prior.
- In some situations, If MOFs have no rings and contain the shortest circuits, the ∞ is presented the shortest circuit's size. (Wang 2006, 19)

3 METAL ORGANIC FRAMEWORK'S NETWORKS

The analysis of MOFs' crystal structure area and 3D-coordination polymers is examined by the topological method and topology descriptors. There are four essential points need to be concerned when using the topological method: (Öhström 2015, 156)

- The structure of MOFs must be clearly determined
- Compared the MOFs' materials to another
- Performing the scientific analysis carefully
- The structure of MOFs is totally new.

There are three aspects of topology that are noticeable named the point symbol, vertex symbol and coordination sequence. The point symbol is utilized to calculate how many nodes in the ring by starting point to shortest ways to return it. The vertex symbol determines how many different ways that the shortest rings are built. The last one is the coordination sequence which means the network from one point to its nearest neighbors and how many of them. Besides, this way also distinguishes the nets which have the similar point symbols and vertex symbols. (Öhström 2015, 156)

3.1 3D networks

During the period of 60s and 70s, that time is the milestone of inorganic structure chemistry, the research article called "Three-Dimensional Nets and Polyhedral" was published by Wells. This study focuses mainly on the geometrical basis of crystal chemistry and the method of the topological analysis of crystal's structure. The advantage of this method is the simplification of structure which is convenient to compare with related structures. (Wang 2006, 101)

In Wells' book, the connectivity, different 3D structure and the topological properties' analysis are mentioned and connected nets of structure based on homogenous sphere packings' definition. This definition is invented by Koch and Fischer where the sphere-packing types are symbolized by the letter k/m/f n. The letter k is interpreted as the number of sphere's contacts, m is the number of edges in a shortest closed path of the graph, f is the symbol of crystal family and n is a consecutive number within a k/m/f class. Years later, this method was under the development by O' Keeffe in who simplified the definition. He used three letters represented for three-periodic nets. (Wang 2006, 101-102)

The 3D network of MOFs introduced in figure 4.

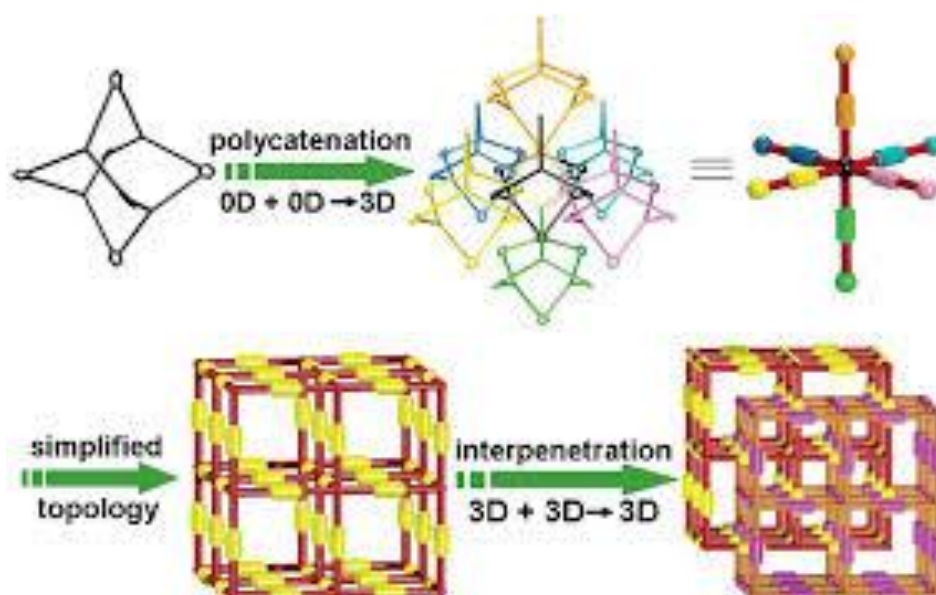


FIGURE 4. The 3D networks of MOFs (Jiang 2013)

3.2 Unitary and Binary nets

The Wells's research still has several limitations because the method extremely simplified the information of network due to the lack of geometrical information of the building blocks of original frameworks. Therefore, the scientist explored the alternative approach in order to meet up the loss of MOFs' information. This approach named Vertex Linked Polygons or Polyhedral (VLPP) which is applicable for complicated linkages especially multiple polygonal building units. (Wang 2006, 108)

Unitary nets are constructed by only one class of polygonal or polyhedral building blocks and considerable structural diversity about the shape and angle which affects their architectures. Meanwhile, the binary nets are comprised of pairs of polygonal building blocks. They are categorized into two binary nets which are the similar type of polygons with different vertices (class I) and types with the share vertices (class 2). The binary nets can create many structures by different ways to combine triangular, square, tetrahedral and octahedral building blocks. The majority of MOFs are generated by this method. (Wang 2006, 118-119)

Figure 5 shows the binary nets examples of different MOFs.

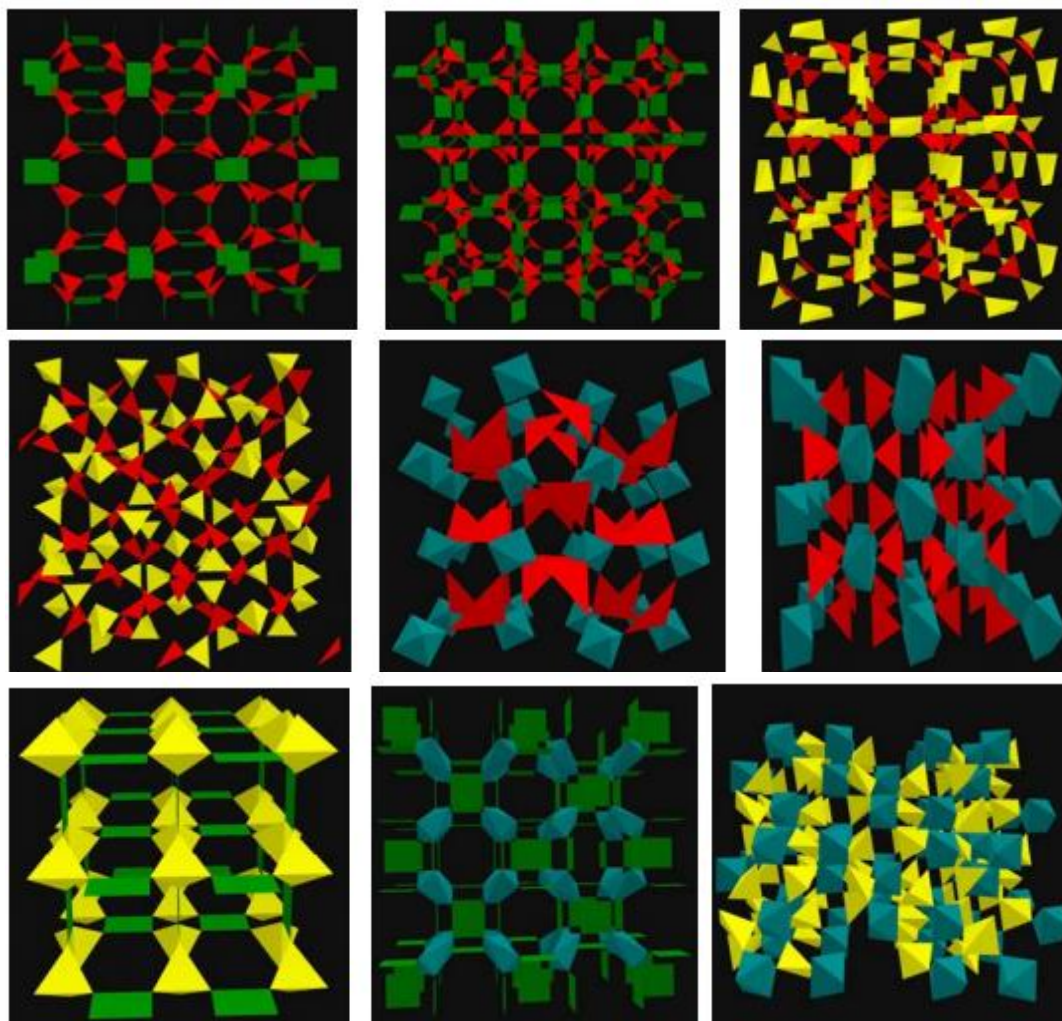


FIGURE 5. Binary nets examples of Different MOFs (Wang 2006, 120)

3.3 Ternary Nets

VLPP solution are applied for the binary nets which builds two types of molecular shapes. However, the research figures out the way to build the MOFs with topologies with higher degree by the way to combine three types of molecular shapes called ternary nets. Therefore, VLPP method is upgraded for three types of polygons. (Wang 2006, 121.)

Figure 6 shows the ternary nets of various MOFs.

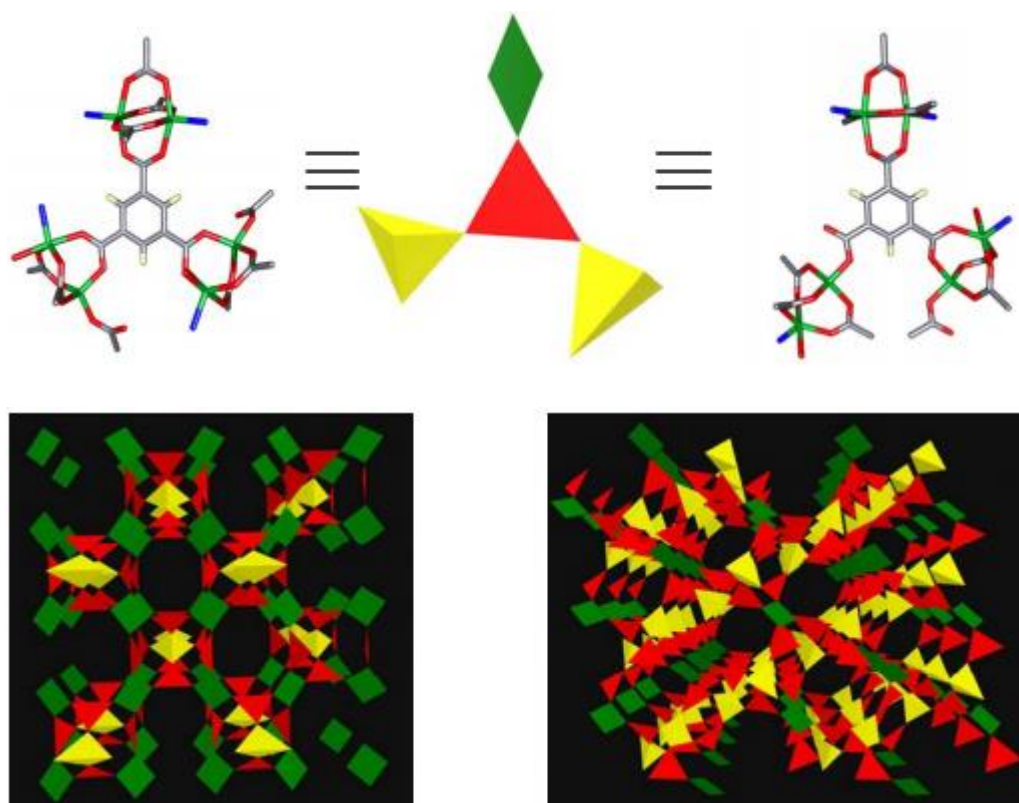


FIGURE 6. Ternary nets examples of Different MOFs (Wang 2006, 125.)

4 SYNTHESIS OF MOFs

There are seven different kinds of synthesis solutions named classical hydro thermal, microwave heating, diffusion, ultrasonic, mechanochemical, electrochemical and spray-drying. Among those, hydrothermal synthesis is recognized suitable used for major MOF's production. There are many conditions affecting on the formation including parameters, solvent, pH levels, molar concentration, temperature, pressure and reaction time. (Raghavan et al 2014, 65-66)

In the previous decades, the design of MOFs' structure based on the geometrical method that contributes a lot of certain success to the creation of large number of functional coordination polymers. For example, 4,4'- bipyridine is built based on the coordination geometry of metal ion. The single metal ions and linear space 4,4' bipyridine has transformed to different superstructures. (Raghavan et al 2014, 65-66)

Figure 7 shows the 4'4- bipyridine with different structures.

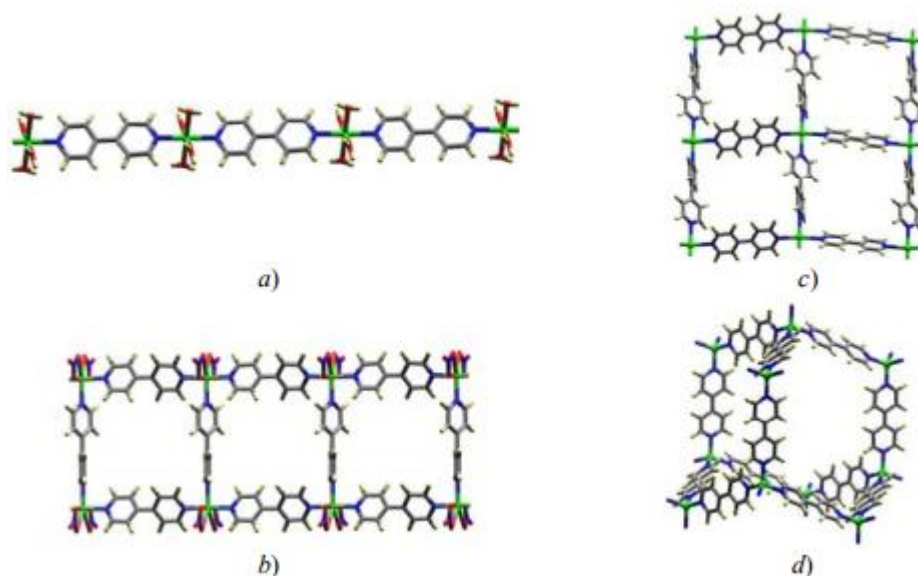


FIGURE 7. 4'4- bipyridine with different structures (Wang 2006, 26)

However, this method still has enormous weakness which is that the pyridyl rings can move as rotation around the metal ions center, so the degree of control over the final structure limitation. Besides, the appearance of special ions invades free space structure that leads to the break of the host framework.

Therefore, a new method called “secondary building units” (SBUs)” has been invented to modify the MOFs' structure. This method was previously applied in zeolite chemistry. After that, this method has

been extended by Yaghi and Eddoudi to rebuild MOFs and create new stable structure. For example, SBUs is used for 1,4- benzenedicarboxylate and 1, 3, 5- benzenetricarboxylate. (Wang 2006, 26-27)

There are four different types of secondary building units which are generally described as $M_2(RCOO)_4$ with dimetal tetracarboxylates as main component. The most popularity of SBUs used in MOF chemistry is SBU I or can be known as paddle-wheel. SBU 1 is applied for more than 1300 crystal structure because of its appropriate accessibility and ubiquity. Moreover, paddle-wheel can be found as Cu, Rh, Ru and Mo. Regarding to SBUs II, III and IV are not used widely comparing to I in the crystal engineering of MOFs. The four types can be applied not only for MOFs structure but also using for node-and-spacer solution. (Wang 2006, 28)

MOFs' structure contains weak bonds leading to structural flexibility under external conditions such as temperature, mechanical pressure, electric field, magnetic field, light, gas and liquid or vapor sorption. (Raghavan et al 2014, 67)

Regarding another property, the scalability plays a significant role for the industrial applications. BASF has been successfully to the large-scale synthesis of MOFs by solvothermal synthesis process. (Raghavan et al 2014, 67)

There are several methods used for MOFs research, it depends on the MOFs' abilities. The morphology, arrangement of atoms and pore structure are determined by X-ray Diffraction (XRD) solution. The surface area, pore width and volume are measured by BET and pore size distribution. The functional groups of MOFs structure are discovered by Infrared spectroscopy. Furthermore, the information of stability and optimal activation temperature are got by Thermogravimetric method. The gas storage capacities, gas adsorption selectivities and diffusivities of gas molecules in MOFs are collected by Gas adsorption technique. (Raghavan et al 2014, 68)

5 APPLICATIONS

MOFs has been used for different types of scientific aspects thanks to the particular properties such as large surface areas, flexible pore sizes, predictable and variable structures. MOFs can be applied for gas storage and separation, catalysis, sensing and proton conduction. Besides, MOFs are clean and renewable materials with long cycle life so that can be used for energy storage materials. (Raghavan et al 2014, 68)

5.1 Sorption Applications

This application has recognized as the important application of MOFs which are able to separate the mixtures of gases that has huge benefits to produce Oxygen purification, natural gas sweetening, carbon dioxide capture and noble gas separation. However, the separation depends on the molecule size and physical features of gases so that it is problematic for the separation process of gas mixture which has the same abilities. (Raghavan et al 2014, 68)

Hydrogen is mentioned as a new candidate of fuel which can be replace for traditional fuels, but its properties is unstable under ambient conditions, so it is not efficient for practical applications. Therefore, MOFs have been attracted to the storage of Hydrogen because of their high capacities that lead to the increase the density of Hydrogen under ambient conditions. (Raghavan et al 2014, 68)

Carbon dioxide has huge negative effect to environment, so it must be controlled. Therefore, carbon dioxide capture method is one of the necessary methods in clean energy applications. MOFs can be used for the CO₂ sorption but at low pressures because the partial pressure of CO₂ is about 0.15 bar which is much lower than atmospheric pressure. (Raghavan et al 2014, 71-72)

Methane storage: methane is the main component in natural gas which can be produced in industrial zone for example biogas plant. The requirement for the CH₄ storage is not only has a huge surface area but also a large pore capacity and the structure contains molecule with low density and can be interacted with CH₄, so MOFs are the best option for the design of methane containers. (Raghavan et al 2014, 70-71)

Last but not least, MOFs can be applied for the removal of harmful gas which release high threats to the natural habitat. There are six different types of MOFs has been public to eliminate eight kind of harmful

gases including sulfur dioxide, ammonia, chlorine, tetrahydrothiophene, benzene, dichloro-methane, ethylene oxide and carbon monoxide. Based on the adsorption capacity of MOFs materials, the suitable MOFs is selected appropriate with MOF-5, IRMOF-3, MOF-74, MOF-177, MOF-199 and IRMOF-62. (Raghavan et al 2014, 76-77)

5.2 MOFs as catalysts

MOFs can be used as catalyst for both industry area and laboratory work. There are three selections for MOFs' ability which are frame work activity, encapsulation of active species and post synthesis modification. Therefore, MOFs can be used as heterogeneous catalysis and it may be developed in the future. In vapor phase reactions, MOFs has low thermal and chemical stability that allows MOFs participate in the reactions over 300°C in industrial scale. For instance, oil refining or petrochemical process. On the other hand, in liquid-phase reactions, MOFs can be more outstanding than zeolites in catalytic reaction specifically under mild conditions. Besides, chemical composition, organic and inorganic building units and bifunctional metal or acid sites for insertion applied iso reticular are the fundamental benefits of MOFs. (Raghavan et al 2014, 78)

5.2.1 Framework activity

Function of MOFs as heterogenous catalysts is using the exchangeable coordination positions around the metal ions. There are two kinds of framework activities which are Lewis acid and Bronsted acid catalysis. With Lewis acid catalysis procedure, the metal center can be removed from ligands under high temperature. When it comes to Bronsted acid catalysis reaction, the MOFs play a catalytic role in oxidation reaction. The products of Bronsted acid can be measured by low temperature CO chemisorption method. (Raghavan et al 2014, 78-80)

5.2.2 Encapsulation of active species

One of the features of MOFs in the catalysis community is able to accommodate another molecule because this compound supplies a huge pore volume that can support or host for the catalytic species. Besides, MOFs are suitable for the encapsulation of active species such as metal complexes or metal nanoparticles because of the porosity of MOFs. MOFs can be capsulation because they support or host for the catalytic species because it can find the location of noncovalent interactions. (Raghavan et al 2014, 80-81)

5.3 MOFs Application for Medicine

There are two reasons to apply MOFs for effective medicine delivery which are the MOFs' size and transformation in functional groups by adjusting the pore size. The hydrophilic pores in MOFs has both charges which are capable of attract the opposite charges in drugs. However, MOFs surface do not contain the non-toxic iron (III) which are nanocarriers for antitumoral and retroviral drugs delivery. Hence, the post-synthesis surface is covered by cyclodextrin molecules bearing iron groups, that coating does not impact the MOF's porosity, adsorption and release capability. Besides, with the various choices of coating leads to many different results forss medicine selection. Cell Walls is natural materials and non-toxic which is used for the synthesis of microcapsules by the linkage of MOFs together. The microcapsules are stable and release small molecules slowly. (Pettinari at al. 2017)

5.4 The Luminescence properties of MOFs

The Luminescent principle of MOFs are worked by the active elements or processes stimulated by organic chromophore. Besides, the MOF's luminescence is able to be changed through metal and organic ligand substitution. For example, $[Ln_2Cl_6(bpy)_3] \cdot 2bipyridine$ is successfully used for the change of the color's emission, the core of MOFs structure in the situation are lanthanides group, the porosity of MOFs can be change by using different types of lanthanide ion but the luminescent properties do not change.

MOFs contains different guest molecules such as chromophores. The MOFs' molecules affect the week connection between ligand and metal center that leads to the change of luminescence spectra. This method can be used for the adjustment of ultraviolet and wavelengths emission by controlling the type and number of guest molecules. (Pettinari et al. 2017)

5.5 Sensing Applications of MOFs

According to the ability of MOFs' tunable luminescent properties, this kind of materials can be used for creating various types of sensors. This sensor is capable of capturing the analyte molecules applied in the detection of volatile organic compounds. Besides, this sensor can increase the level of emission in analytic gases at room temperature. When the temperature changes that lead to the intensity changing but the peak position of the emission still remains stable. The biosensor is also regarded to the luminescent MOFs. For example, MOF 5 can be applied for specific sensing of bovine serum albumin. The other groups can be added into MOFs structure by post synthesis method. (Pettinari at al. 2017)

6 ZEOLITIC IMIDAZOLATE FRAMEWORKS (ZIFs)

Zeolitic imidazolate frameworks (ZIFs) is a typical class of metal organic frameworks, this material includes imidazolate linkers and metal ions. The structures are identical to the aluminosilicate zeolites. ZIFs' porosity and chemical stabilities have a huge potential for industrial materials. In the past five years, the emerge of ZIFs has been attracted and developed by many analysis method and study also the laboratory experiment. The application of ZIFs can be applied for different aspects which are gas separation, catalysis, sensing, electronic devices and drug delivery. Besides, the new development of ZIFs material has been succeeded with the synthesis into both powder and membrane. (Chen et al. 2014, 1-2)

In addition to the properties of ZIFs, this material is the benefits' combination of not only MOFs but also zeolites. Because ZIFs are sub family of MOFs and ZIFs' structure also contains zeolite, this material possesses ultrahigh surface areas, exceptional thermal, chemical stabilities, unimodal micropores, high crystallinities and adundant functionalities. Thus, those properties make ZIFs be able to use in many industrial fields. (Chen et al. 2014, 1-2)

The general structure of ZIFs can be symbolized as Metal-Im-Metal in which metal can be represented as metal cation such as Zn, Co and so on while Im is the symbol of imidazolate linker. The metal cation and imidazolate linker can be connected by the self-assembly method. ZIFs have tendency to create zeolite like topologies but it is not similar to the tradition zeolites forms. (Chen et al. 2014, 1-2)

Figure 8 shows structure of Different Zeolitic Imidazolate Frameworks.

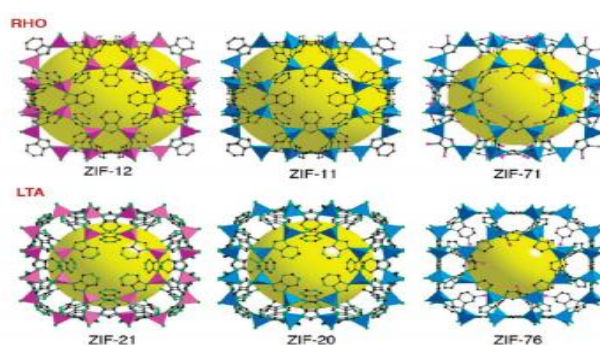


FIGURE 8. Structure of Different Zeolitic Imidazolate Frameworks (Phan et al. 2009)

7 SYNTHESIS OF ZIFs

The process of Zeolitic Imidazolate Frameworks' manufacture is based on the traditional method which called hydrothermal approach. The conditions for the production's principle are the requirement of temperature up to 200°C as well as the reaction's duration in range of at least 8 hours to a few days. The products of ZIFs are classified as powder and film or membrane status which depends on the purpose of usage. (Chen et al 2014, 3)

Figure 9 illustrates the synthesis method of ZIFs.

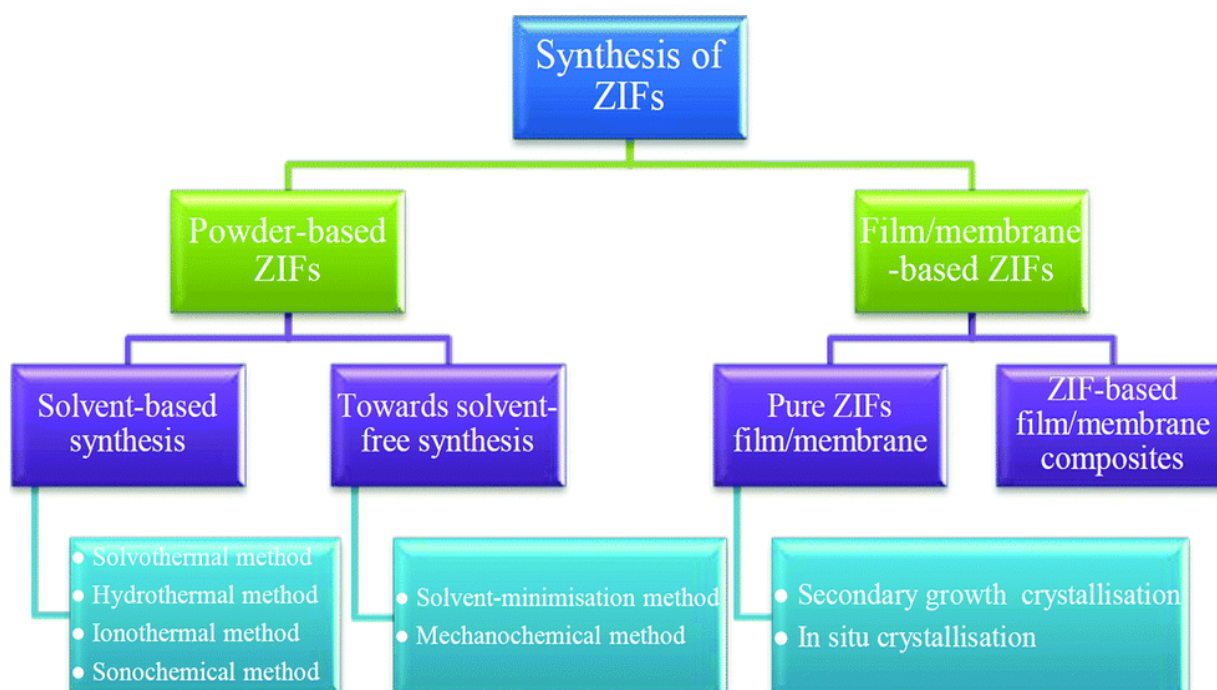


FIGURE 9. The schematic graph of ZIFs' synthesis (Chen et al. 2014, 3)

7.1 Synthesis of Powder ZIFs

The synthesis's principle of powder based ZIFs is regarding to the separation from the mixture by the elimination of solvents or impurities. There are two different methods for the production are solvent and non-solvent synthesis. (Chen et al. 2014, 3)

7.1.1 Solvent – based synthesis

This method is comprised of four different methods to create ZIFs powder which are solvent thermal, hydro thermal, Ionothermal and sonochemical synthesis. (Chen et al. 2014, 3)

Regarding to the solvothermal method in which the organic solvent is chosen as the role of reaction medium. Especially, methanol is the significant and popular organic solvent applied in the manufacture's procedure. In 2006, this method is created by Chen's team who produced ZIF crystals called MAF. After that, Yaghi applied this method into the creation of twelve different ZIF crystals namely, ZIF 1 to 12. Besides, N,N- dimethylformamide (DMF), N,N diethylformamide (DEF) and N-methylpyrrolidine (NMP) are the organic solvents applied in the research. (Chen et al. 2014, 3-4)

However, the solvo thermal synthesis has several weaknesses which influence on the manufacture's efficiency. The problem is the organic solvents which are extremely expensive, inflammable property and also polluted to the environment. Therefore, the method has been changed by the combination between metal ion and methylimidazole (MIm). After that, the ZIFs material is collected by the centrifugation happened in approximately five minutes and 6000 rpm. But the issue is that the MIm is excessed during the process so the product is wasted. Therefore, the ratio between metal cation and MIm should be controlled by the way using the additives solution in the process. The additive avoid MIm to create ligand. For example , Miyake produce ZIF under ammonium hydroxide environment at room temperature, the ammonium hydroxide maintain the ration between Zn^{2+} and MIm that lead to reduce the waste. Hence, this method can be used in industrial scale because of its cost-effective strategies. (Chen et al. 2014, 4)

The third method is Ionothermal synthesis which has been applied and improved in ZIFs materials. This method was recognized initially by Morris and his partners. In the synthesis process, Ionic thermal method allows green solvents and eutectic mixture participating to produce ZIFs. Green solvents such as ionic liquid has a huge impact which prevent the competitions between the solvent framework and template framework during the hydrothermal process. This method has huge attraction by many scientists because it can be applied for the open system also the green solvent is probably reused. (Chen et al. 2014, 4)

Last but not least, the sonochemical synthesis is also the method to create ZIFs powder but using the nucleation instead of the normal oven heating method. This method emits high temperature, pressure.

During the process, the ultrasound radiation is applied so that the materials contain bubbles which are generated and known as acoustic cavitation. The products are created by the sonochemicals synthesis having smaller and narrow particle size distribution than the other manufactures. For example, according to Seoane's article, the pure ZIF 7, 8, 11 and 20 crystals were created under the ultrasound radiation's condition lasting in 6-9 hours, this process also requires a power of 110W, frequency of 47 kHz at 45-60°C temperature. (Chen et al. 2014, 5)

7.1.2 Non-solvent synthesis

It is undoubtedly that the importance of solvent solutions involved in the ZIF's manufacture which results in the affordable capital as well as the eco-friendly issue. Nevertheless, if the management of both the imidazole sources and solvent washing is not carefully, the excess of those solutions can be happened and leads to the inefficient production of ZIFs. Therefore, there are two new kinds of ZIFs fabrications methods which are solvent-minimisation and mechanochemical synthesis. (Chen et al. 2014, 5)

The first solution is minimized-solvent method which has been researched in these years. The method has been achieved successfully by applying steam assisted conversion approach. For instance, ZIFs 8 and ZIF 67 can be produced by minimizing solvent method which means using the solid phase instead of liquid. The solid phase contains metal salts and excess ligands positioned in a small Teflon cup which covered by water vapour, the temperature demands at 120°C for a day. The water vapour plays a role as the agent in the synthesis process. (Chen et al. 2014, 5)

Besides, Friscic has developed a new method named accelerated aging which based on the geology and minerals. This method can exploit thoroughly the mobility function of molecules in the synthesis process. The mechanism principle is based on the proton transfer which defined by Friscic. The catalytic salts can transform the metal oxide converting to ZIF material by using the acceleration. In the process, the metal oxide and imidazole ligand are combined together with ammonium sulfate as catalyst placed in an open vial underground at 45°C and 98% moisture for a few days. After that, the close packed ZIFs were collected through washing and drying step. For example, at the first time, Friscis applied this method in order to produce ZIFs with imidazole, 2-methylimidazole, 2-ethylimidazole and benzimidazole without solvent. (Chen et al. 2014, 5)

The last solution is mechanochemical manufacture which theoretically defined as the breakage of solid materials in order to convert them into powder with small size particles by the grinding machine. Additionally, the participation of several added liquid solution also plays an important role for the efficient process. Because of its benefits, this method can be applied in the non-solvent synthesis of ZIFs. For example, in 2006 the first manufacturing process was happened between the non-porous ZnO and Imidazole (IM) converted to $\text{Zn}(\text{IM})_2$. (Chen et al. 2014, 5-6.)

Figure 10 introduces the mechanochemical synthesis of ZIFs.

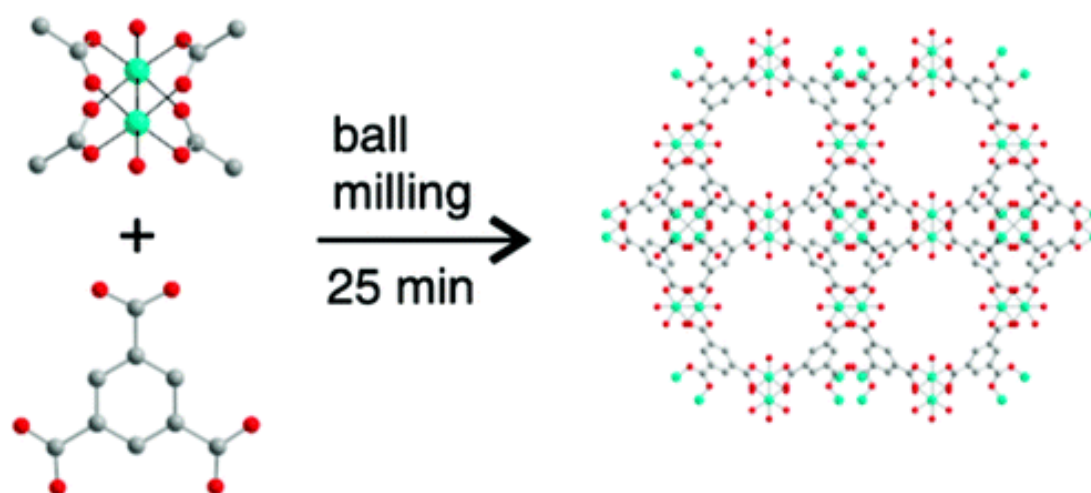


FIGURE 10. The mechanochemical synthesis of ZIFs (Klimakow et al. 2010)

7.2 Synthesis of Film/Membrane ZIFs

Except for the synthesis of Powder ZIFs, their product can be formed as films or membranes. This product can be used in several area such as gas separation and chemical sensors because of the special abilities especially molecule-sized porosity and easy handling. There are two methods to approach the manufacture of ZIFs membranes which are Pure ZIF films or membranes and ZIFs based films or membranes composites. (Chen et al. 2014, 6)

7.2.1 Pure ZIF films and membranes

The scientists have figured out different kinds of ZIF films and membranes' production which can be fundamentally classified in two different types named secondary growth crystallization and in situ crystallization. (Chen et al. 2014, 6)

7.2.1.1 Secondary growth crystallization

The first method to prepare membranes is called secondary growth crystallization which is comprised of two directions. These ways are depositing the crystal seeds through rubbing, dip-coating, thermal seeding or repeated growth and then pre-treating the support by the involvement of reactive seeding or organic groups. During the process, the growth of seeds fulfills the gaps inside the seeds that resulting in the formation of membrane. The considerable benefit of the method is the membrane can be controlled. Besides, the membrane thickness and the structure can also be modified so the membrane performance can be enhanced better. In addition to the secondary growth crystallization methods, the product can be gained with high quality ZIF membranes because of the improved interaction between ZIF crystals and the support. In recent years, the scientists researched to develop the new approaches such as reactive seeding, pre-coating the polymer or organosilane binder, infiltrating precursors and microwave assisted seeding. (Chen et al. 2014, 6)

The removal of the weaknesses such as the cracks and intercrystalline defects are performed by reactive seeding. The typical example is that a ZIF-8 membrane was created by this method where the in situ crystallization was used to support the loosely packed crystals. After that, the creation of compact seed layer by this method. During the process, the secondary growth method is formed ZIF 8 membrane as a continuous and defect free reaction. (Chen et al. 2014, 7)

Figure 11 shows ZIF 8 membrane formation by reactive seeding.

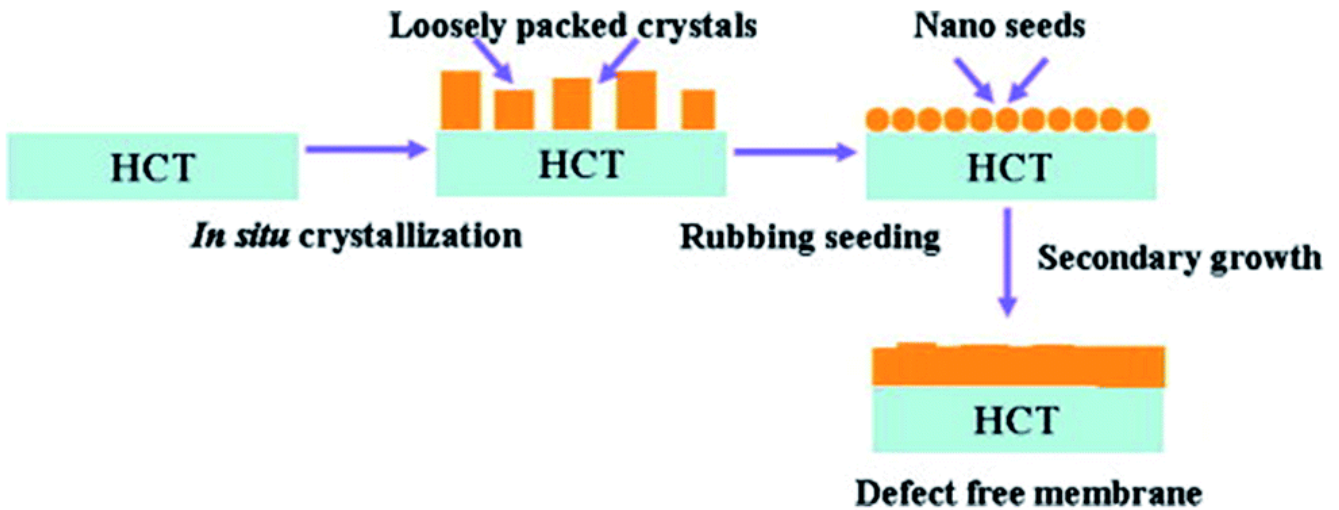


FIGURE 11. ZIF 8 membrane formation by reactive seeding. (Chen et al. 2014, 6)

The next method is Pre-coating polyethyleneimine (PEI) solution has been employed successfully in the production of ZIF 7 membrane. The PEI solution can combine with the Zinc ions at the surface of the nanoseeds which cause them compatible. Therefore, PEI is able to improve the connection between the seeds and the support via hydrogen bonding connections. Moreover, the infiltrating precursors solution is recognized as a seed and nutrient layers with the function of dense and stable creation for the ZIF membranes. With the participation of the microwave assisted seeding, this is a new approach to create the high packing density rapidly in a few minutes. Furthermore, the polymeric support is an alternative way to enhance the linkage between ZIF crystals and the support because of the high affinity between them. However, it is difficult to control the membrane thickness on the submicron scale by this method. (Chen et al 2014, 7.)

7.2.1.2 In situ crystallization

The second method that generating ZIF films or membranes is in situ crystallization in which the support can be modified by one step or one pot solvothermal or hydrothermal synthesis and the polycrystalline layer is increased on the plain without the involvement of seeding growth step. Many researches have been pointed out that the production of ZIF films or membranes which happens efficiently when the substrate must be modified before going to the situ crystallization, counter-diffusion-based in situ crystallization and solvent evaporation-based in situ crystallization. (Chen et al. 2014, 7)

The benefit of the initial modification of substrate is the achievement of ZIF membrane in continuous process. For example, ZIF 7 and ZIF 8 can be synthesized easily by support modification such as heating

and fast evaporating. On the other hand, the solvothermal synthesis method is that using the chemical 3-aminopropyltriethoxysilane (APTES) in situ crystallization. The role of APTES is promote the heterogeneous nucleation and generate the membrane by using the covalent bond in APTES structures. (Chen et al. 2014, 7)

ZIF membranes is also fabricated by a counter diffusion method which mainly separate the metal ions from ligand. This method allows the membranes capable of self-recovery several times so it can be recycled and costly. For instance, ZIF 8 membrane is generated by counter diffusion synthesis according to Xie et al. In this process, the two solutions were added to inner and outer volumes of the tubular support. In addition, Kwon et al also applied this method to produce ZIF 7 and SIM 1 achieved. (Chen et al. 2014, 7)

Shah et al released the method called solvent evaporation- based in situ crystallization according to the concept of evaporation induced crystallization of Ameloot et al. This method is successfully applied for the manufacture of ZIF 8 membrane with the support of α -alumina. (Chen et al. 2014, 7)

Figure 12 describes the solvent evaporation method.

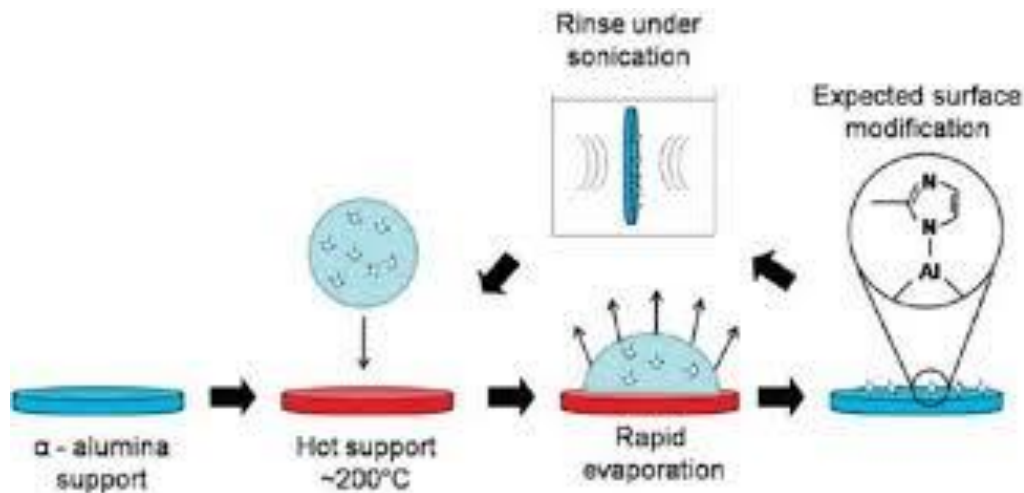


FIGURE 12. The solvent evaporation method. (Chen et al. 2014, 8)

7.2.2 Synthesis of ZIF based film/membrane composites

The ZIF based film or membrane composites can be prepared by the appearance of polymers because of the connection between polymers and ZIFs and the impact of molecular sieving leading to the product called mixed matrix membranes (MMMs). A qualified MMMs have well dispersed particles as high as possible. However, there are several problems need to be concerned such as the interactions between polymeric phases and inorganic phases in ZIFs materials consequence in many issues. Namely, the synthesis of ZIF as well as the controllable dispersion of ZIFs with the presence of polymer. The MMMs fabrication process is comprised of several steps which are solution blending, dip coating and solution casting. There are some necessary conditions for the production of MMMs such as the selection of permeability and acting selectivity of ZIFs as well as the concentration ratio of ZIFs and organic polymer solution. The mixture of ZIFs and organic polymer solution are stirred together and the result is called the homogeneous suspension which is coated with substrate to create membranes under the vacuum conditions with high temperature. After that, the membrane is set to cool under the room temperature. (Chen et al. 2014, 8)

Figure 13 shows the MMMs' synthesis process.



FIGURE 13. The MMMs' synthesis process (Chen et al. 2014, 9)

8 PHOTOCATALYSIS

In 1972, the two scientists named Fujishima and Honda explored the phenomenon of photocatalytic separating of water on a TiO_2 electrode with the influence of ultraviolet (UV) light. This moment became the open of new breakthrough for the chemical science. However, this research was not acknowledged by the other electrochemist because at that period, the idea that light could be utilized as an energy source was impossible. Those scientists could not support that the water able to be created under the low voltage because of water electrolysis happened at minimum 1.5V. In the following years, with the research and development of scientist on the photocatalysis, this method has been accepted. After that, there were many researches performed by different experts such as the application of photocatalysis contributing to “energy renewal and energy storage”, the popularity of TiO_2 used for wastewater treatment and air treatment to destroy the organic compounds. (Saravanan et al. 2017, 24)

The term photocatalysis can be defined as the interaction of photochemistry and catalysis. This method includes two parts which are the prefix photo in Greek language means light and catalysis happens when a substance attends to the reactions with substances do not occur to the reaction but it can affect the rate of chemical transformation. The photocatalysis is the light and catalysts which enhance the chemical reaction. That results in the speed up of chemical reaction and the reduction of energy used for the process. In other words, the photocatalysis can be understood as “catalysis driven acceleration of a light induced reaction”. (Saravanan et al. 2017, 25)

There are two different types of photocatalysis process which are homogeneous photocatalytic and heterogeneous process. With homogeneous photocatalytic process, this catalyst, reactants, and products is the same phase while heterogeneous where the phase of the catalyst differs from that of the reactants. The catalysts are mainly the metal complexes, under the light and temperature condition, metal complexes create hydroxyl radicals and then it reacts with organic compound in order to the breakage of toxic matters. (Saravanan et al. 2017, 25)

The influence of photocatalysis is undoubtedly because of its contribution to the chemistry aspects. This method can be applied for the degradation pollutants in wastewater, the generation of hydrogen, purification of air and the antibacterial activity. (Saravanan et al. 2017, 25)

8.1 Photocatalytic mechanism

Fundamentally, the photocatalytic principle depends on how wavelength or light (photon) energy and the catalyst behave. The popular catalyst is the semiconducting materials which has a special electronic structure. Its ability is determined by a filled valance band and vacant conduction band. In the reaction process, under the light, the catalyst is stimulating to create the redox reaction. (Saravanan et al. 2017, 26)

Figure 14 shows photocatalytic mechanism.

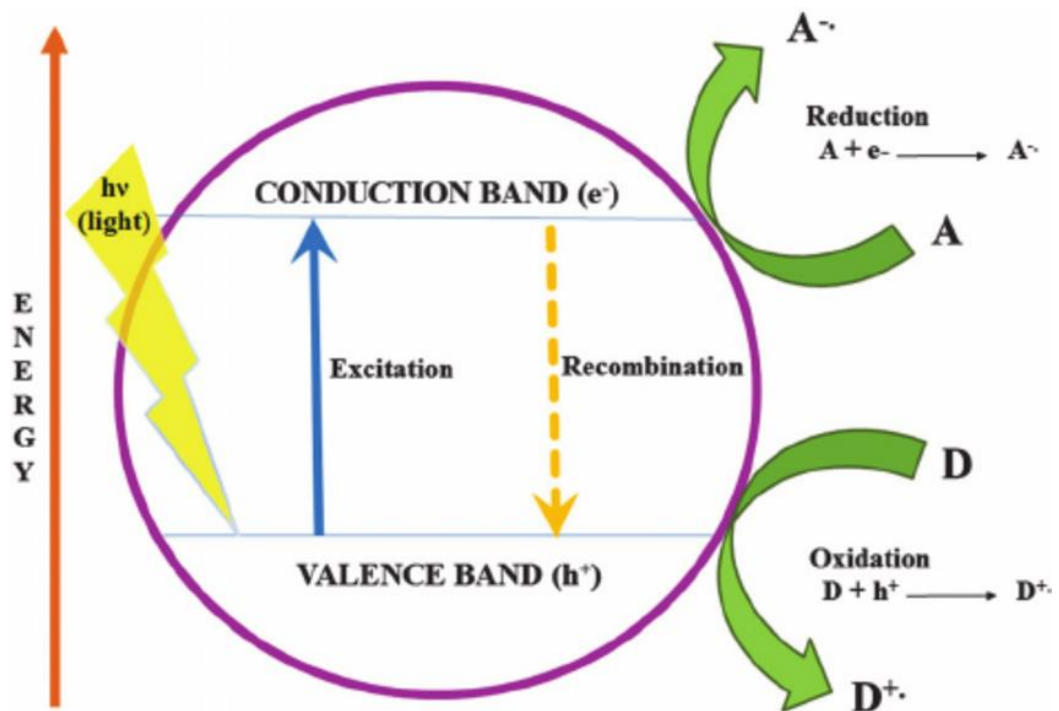


FIGURE 14. Photocatalytic Mechanism (Pal et al. 2015)

There are several steps which describe the process of the photocatalysis. Initially, when the light enters the surface of the catalyst with the energy of the incident ray is higher than the bandgap energy of the catalytic materials. The result is that the electrons of the valence band are affected and transferred to the conduction band area in the semiconductor. After that, the valence band contains the holes which their role is to oxidize donor molecule and react with water to produce hydroxyl radicals. This radical is the strong oxidizing for the degradation of pollutants. In the conduction band area, the superoxide ions are the formed by the reaction between elections and dissolved oxygen. (Saravanan et al. 2017, 26)

Besides, as mentioned above, the photocatalysis consists of two main reactions which are oxidation and reduction. Regarding to the oxidation reaction, it means that water is contained in the surface of the photocatalyst known as adsorbed water. Water reduces the positive holes in the valence band and then under the light irradiation condition, the electrons from the valence area move to the conduction band. Consequently, the hydroxyl radicals are formed which react with organic compounds in the dyes. After that, the organic matter is decomposed to create carbon dioxide and water. (Saravanan et al. 2017, 27-28)

In the reduction process, the oxygen in the air will react with conduction band electrons to form superoxide anions. After that, the superoxide anions transform to hydrogen peroxide and then immediately change to water as the final. With the high concentration of organic matter, the quantity of positive holes also increases. (Saravanan et al. 2017, 27-28)

Figure 15 illustrates the oxidation and reduction process.

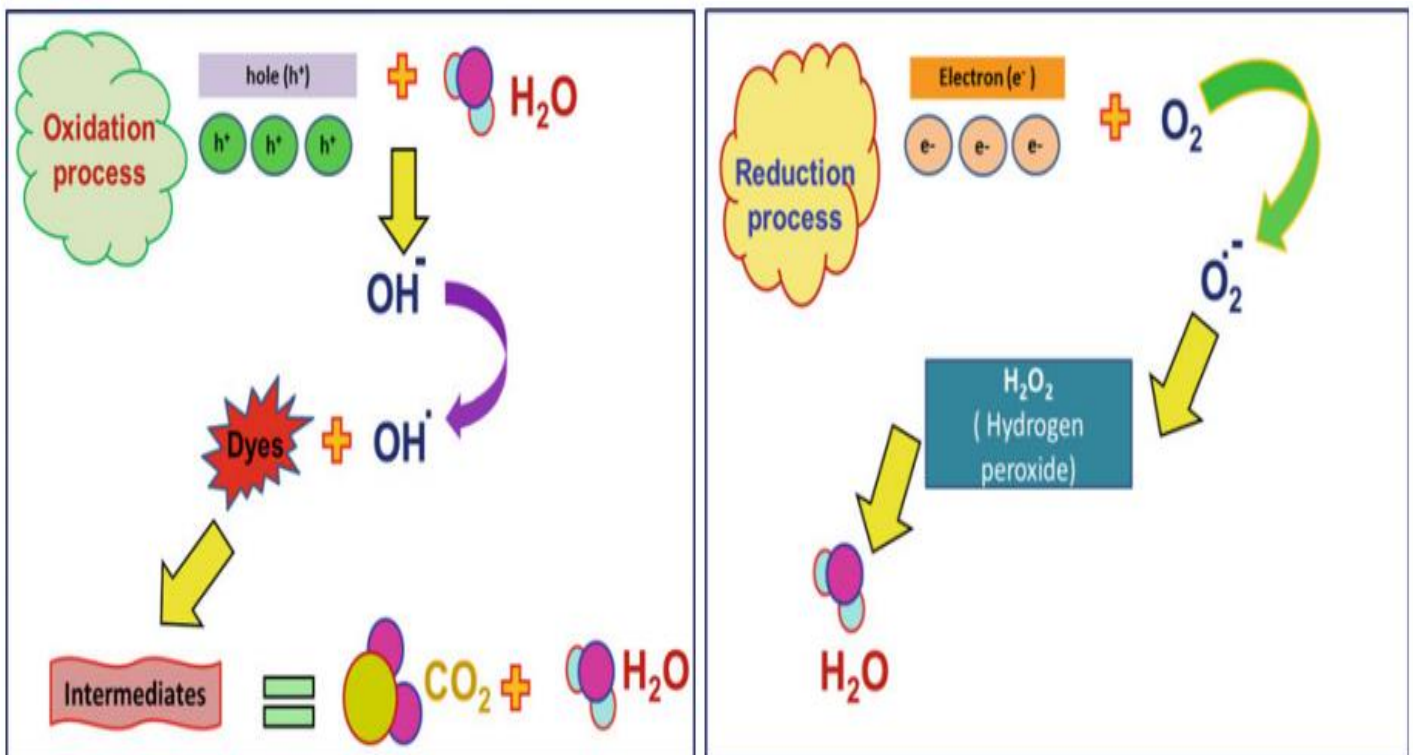


FIGURE 15. The oxidation and reduction process (Saravanan et al. 2017, 27-28)

8.2 Factors Affecting to The Photocatalysis

There are many different parameters need to be concentrated during the process of photocatalysis such as the structure, shape, size and surface area of the catalyst, reaction temperature, pH level, light's ability, the amount of catalyst and wastewater's concentration. (Saravanan et al. 2017, 29)

8.2.1 Crystal structure, shape, size and surface area of catalyst

First, the catalyst's structure has a huge impact for the photocatalytic efficient activity. For example, the TiO_2 material contains three phases such as anatase, rutile and brookite. However, according to Khan's research, the most effective factor is anatase phase because of its stability, the high degree of hydroxylation and the ability of absorption. Moreover, the shape of catalyst also the main factor that influence on the reaction efficiency. The report of Saravanan et al introduces that the shape of spherical ZnO gets the higher efficient than the spindle and rod shaped ZnO when using as the same amount and under the UV light condition. Besides, the smaller the size of catalyst is utilized, the higher the rate of volume in the surface is which lead to the massive number of atoms are accumulated on the surface of the catalyst. This factor also boosts the number of active sites and the contacted surface between catalysts and reactants. (Saravanan et al. 2017, 29)

8.2.2 The effect of temperature

There are many researches on the temperature's behaviors during the photocatalysis reaction. Chatterjee and Dasgupta demonstrated that when using TiO_2 material as the catalyst, the optimum range of reaction temperature that the process can operate efficiently are 20-80°C. When the temperature increases over 80°C that lead to the electron hole recombination as well as desorption process so the photocatalytic activity decrease. On the other hand, when temperate is at 0°C, there is increase on photocatalytic activation, this temperature range depends on the activation energy of catalysis material. (Saravanan et al. 2017, 29-30)

8.2.3 The effect of pH level

The pH level is also the important factor to the photocatalytic mechanism. It means that the rate of reaction depends on the electrostatic interactions between charged particles and the contaminants. For

example, the Shourong's report shows that the pH influence on the elimination of organic pollutants in water. In this process, the photocatalyst used for reaction is TiO_2 which use for Reactive Blue 4. The reaction was performed under different pH level adjustment. The results introduce that in the acidic solution ($\text{pH} < 5$), the degradation efficiency decreases because the high concentration proton prevent the degradation of dye. Moreover, the degradation growth in the alkaline environment ($\text{pH} 11-13$) because of the hydroxyl radical rapidly scavenged and it can not react with organic pollutant. The alkaline medium ($\text{pH} = 10$) is the perfect condition for the reaction because the appearance of hydroxyl ion which remove the product of photodegradation reaction process. (Saravanan et al. 2017, 30)

8.2.4 The effect of light intensity

The light intensity is also the main factor in order to affect the degradation rate of the photocatalytic process. The ratio of the reaction's rate to the radiation absorption 's rate is given by quantum yield which also knows as the absorption of light quanta. Besides, with usage of different wavelengths of the light source, the rate of photocatalytic reaction also behaves variously. Malato et al used the TiO_2 as catalyst and the reaction used different light level. TiO_2 has a huge bandgap energy (3.2 eV) so it allows to absorb in every UV zone. Besides, the report also pointed out that the change of the TiO_2 degradation rate under different light intensities. Particularly, the reaction rate decreases under the high intensity light irradiation because of the increase of the electron hole recombination. Meanwhile, the excess of light intensity causes the promotion of electron hole recombination leading to the decrease in the reaction rate. (Saravanan et al. 2017, 30-31)

8.2.5 The effect of catalyst's amount

The influence of catalyst is also important for the photocatalytic degradation rate. In case of the increase of catalyst's amount, the quantity of active sites on surface also increases that leads to the more production of hydroxyl radicals and oxygen radicals. However, if the amount of catalyst is over the allowable concentration, there is the decrease in the light penetration contacting to solution so the efficiency of the photocatalytic process also reduced. (Saravanan et al. 2017, 31)

8.2.6 The effect of contaminants' concentration in wastewater

Last but not least, the amount of pollutants is also considered as the main issue which affect the rate of the degradation. Many reports have shown that with the usage of the same catalyst happened in the one general condition, but the concentration of pollutants can be adjusted with different values that results

in the various reaction time in the photocatalytic process. For example, the article of Kiriakidou et al illustrated that he used the TiO_2 as the catalyst and performed the operation at the at similar conditions with various change of Acid Orange 7 's concentration. The results were that the process reached to the totally degradation rate at the concentration range (25-100 g/ml) while the concentration from 200 – 600 g/ml, the rate tends to decrease. (Saravanan et al. 2017, 31)

8.3 The pros and cons of Photocatalysis

Mentioning the significant benefits of the photocatalysis method, the first positive point is that this is an alternative method in the industrial area for the catalytic process which can be applied instead of ion exchange method or ultrafiltration method. This is a cost-effective method because of the high capacity when using, recycle catalyst and free solar energy. During the process, this method also produces the harmless product unlike the other treatments. Besides, the photocatalytic can be also applied in the wastewater streams containing the variety of toxic substances. Moreover, the conditions including the chemical using for this process are mild and also the reaction demands a short time. Finally, the process can reduce the pollutions effectively and be applied for the manufacture of hydrogen, gaseous phase and aqueous treatments. (Saravanan et al. 2017, 32)

However, there are several limitations affecting to the reaction efficiency such as the transfer of the interfacial charge, the charge separation's improvement and finally the prevention of the charge carrier recombination. (Saravanan et al. 2017, 32)

9 FREE RADICALS

Free radicals are the unstable compounds which contain the unpaired electrons. The unpaired electrons are extremely reactive and unstable that lead to the fact that the free radicals tend to steal electrons from other molecules. The molecules which is stolen is damaged and transformed to free radicals themselves. This process is called oxidation reaction and the electrons are stolen which cause the vicious chain reaction. Free radicals also play a vital role in the biological aspects as well as different type of diseases. (Norman et al. 2009; March 1992)

The first radical was predicted in the living body by Professor Moses Gomberg in 1900. It was supposed that the system of body contained triphenyl methyl radical but he did not know how detect this free radical. In 50s, the theory of free radical of oxygen toxicity was published by Gershman according to the ability to create free radicals. In 1954, the free radicals had been recognized by Commoner's research that the free radical was existed in living body. In 1977, the report of Mitall and Murad introduced that the formation of OH radical. After there has been many scientists who research and discover a lot of free radicals as well as their characteristics. (Phaniendra et al. 2014)

9.1 Reaction mechanism of free radicals

There are four main types of free radicals' reaction which are abstraction, addition, combination and disproportionation and rearrangement. In the abstraction reaction, the free radicals react with saturated organic compounds by separating an atom from carbon. The selectivity of free radicals depends on dissociation energy of C-H bond and effects of polar. The rate of abstraction process inclines while the bond dissociation energy declines. (Norman et al. 2009; March 1992)

The example is shown in figure 16.

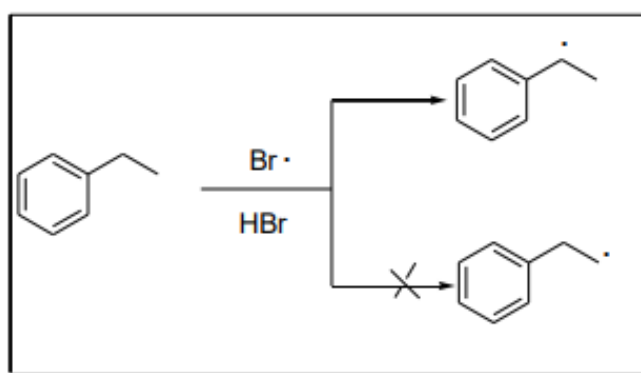


FIGURE 16. The reaction of organic compounds and free radicals (Norman et al. 2009; March 1992)

During the addition reaction, the free radicals is added to the organic compounds which contain C=C double bonds. For example, when the radical X reacts with organic compound with the structure CH₂=CHR, then X is added to the CH₂- part and it takes electron from CHR- part, the product forms X-CH₂-C[•]H-R. (Norman et al. 2009; March 1992)

Regarding to the combination and disproportionation, the two free radicals are reacted together by the method dimerization or disproportionation. The rate of this reaction is extremely high and it does not require much activation energies. (Norman et al. 2009; March 1992)

The reaction's example is shown in figure 17.

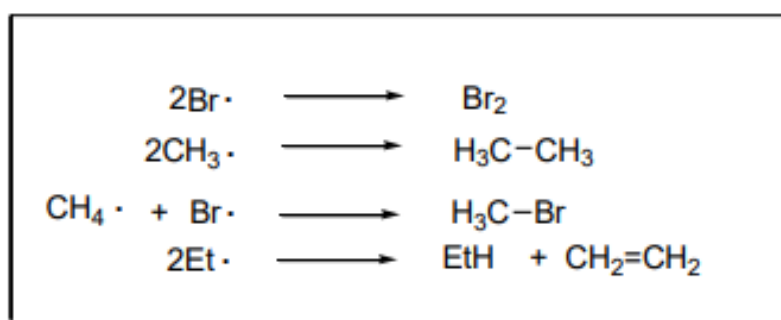


FIGURE 17. The reaction between two free radicals. (Norman et al. 2009; March 1992)v

The final reaction is called rearrangement that mean free radicals are known rearrange in certain condition. The compound contain free radical will transform to create new stable substance (Norman et al 2009; March 1992). Figure 18 shows the the arrangement of organic compounds with catalyst.

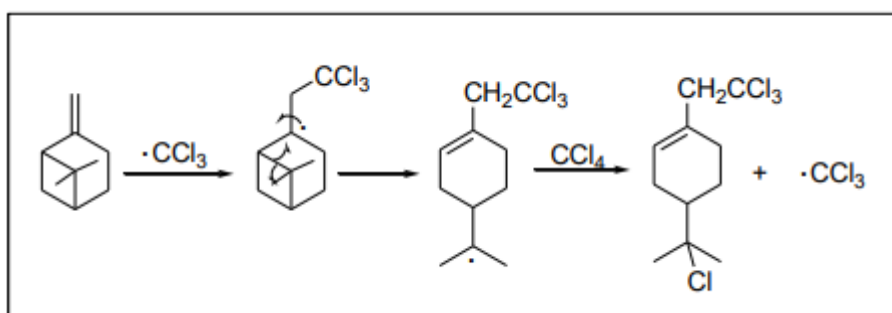


FIGURE 18. The arrangement of organic compounds with catalyst (Norman et al. 2009; March 1992)

9.2 The production of free radicals

There are three general ways which applied for the manufacture of free radicals. The first method is thermal generation. During the process, the two kinds of substances are mixed together under the appropriate temperature. The combination of two compounds will create the strong bonded products and release the free radical at the same time. The next method is called photochemical generation, in this process, the light is used to break the substances in case of the light's wavelength energy which are higher than the bonding force. Besides, the electronic excitation of molecule also results in the free radicals. This method can be applied for the transformation of alkyl nitrite or hypochlorites into alkoxy radicals. The last one is the redox production which consists of the oxidation and reduction reaction. In the process, the electron transfer from one to another by the donation of compound and the gained electron of another compound. The result is that the covalent bonds are broken and releasing the free radicals. (Norman et al. 2009; March 1992)

Figure 19 shows the examples of thermal, photochemical and redox generation reaction.

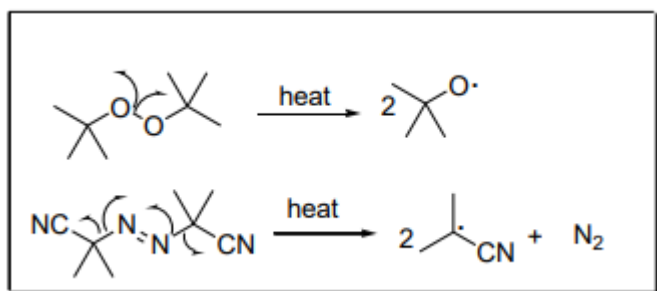


FIGURE 19a. Thermal generation reaction

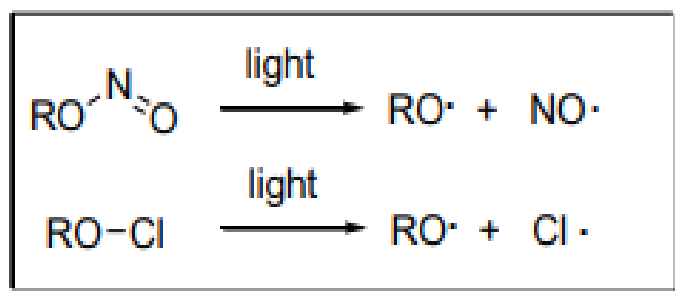


FIGURE 19b. Photochemical generation reaction

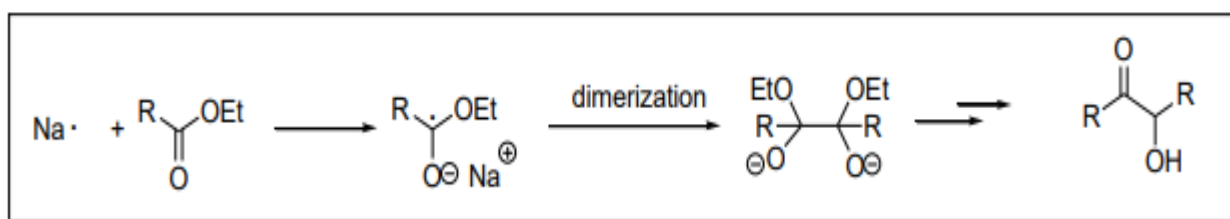


FIGURE 19c. Redox generation reaction (Norman et al. 2009; March 1992)

10 EXPERIMENT EXECUTION

The aim of the laboratory experiment includes the synthesis performance of ZIF 67 (Zn, Co). The usage of ZIF 67 as the photocatalyst to create free radical, after that this free radical is a strong oxidant which will destroy the dye color in water in the case Congo red. Thereafter, the fluorescence technique is applied to analysis the radical under the ultra violet condition. The last experiment identify which free radical will affect to the destruction of dye color and the mechanism of reaction.

10.1 Preparation

TABLE 1: The necessary chemicals for the experiment

| Chemicals | Mass | Volume |
|--------------------|--------|--------|
| 2-methyl imidazole | 0.02 g | |
| Methanol | | 200 ml |
| Ethanol | | 200 ml |
| Congo red | | 500 ml |
| Terephthalic Acid | | 50 ml |
| KI | 20 mg | |
| Benzoquinone | 0.2 g | |
| Iso Propanone | | 50 ml |

TABLE 2: The necessary equipment for the experiment

| Equipment | Volume |
|------------------------------|---------------|
| Pipette | 10 ml, 200 ml |
| Beaker | 200 ml |
| Graduated Cylinder | 500 ml |
| Volumetric Flask | 1000 ml |
| Heating and Stirring Machine | |
| Halogen Lamp (160W) | |
| Centrifuge | |
| Oven | |
| Microwave | |

10.2 Procedure

In this laboratory experiment, there are three experimental sections named the manufacture of ZIF 67 and then using this material as the photocatalyst in dye (congo red) in order to detect the free radicals. After that, the second one is the determination of hydroxyl radicals by fluorescent technique with UV light. Finally, the discovery of radical scavenging mechanism.

10.2.1 The fabrication of ZIF 67 as well as its function as photocatalyst in dye

ZIF 67 is produced by solvent thermal method. In the process, a 2-methylimidazole solution with 16 mmol was added to 100 ml methanol. After that, the metal mixture includes 0.8 mmol Cobalt (II) Nitrate Hexahydrate and 3.2 mmol Zinc Nitrate Hexahydrate was poured into the previous solution. Thereafter, the total solution was heated by microwave in approximately 10 minutes. The product was added into ethanol solution to eliminate the impurities by centrifuge 6000 rpm in ten minutes and repeated in 3 times. The gained substance was heated back in the oven in 16 hours before the ZIF crystal was performed to appear.

Turning to the next phase, the congo red was prepared by distilling 0.01 g its substance into 100 ml water in order to the congo red solution, the Congo red was stirred under the dark environment in around 60 minutes then 10 ml of sample was brought to measure absorption level. After that 50 mg of ZIF 67 was mixed with the congo red solution. The mixture was stirred under the mercury light (160W), each 30 min, 10 ml of sample was measured to gain absorption spectra (wavelength 500 nm).

10.2.2 Determination of hydroxyl radicals

The florescent method is utilized for the determination of hydroxyl radicals intensity. 25 ml of ZIF 67 was transformed to 50 ml terephthalic solution (0.5 mmol), with the involvement of base solution, these solutions were combined to produce 2-hydroxyterephthalic acid under a 160W mercury lamp which was placed 150 mm far from the solution surface. The sample was removed in every 15 minutes. It is noticeable that, in order to ensure the process happened, the concentration of terephthalic acid was less than 10^{-3} M.

10.2.3 Determination of radicals with the participation of Potassium Iodate (KI), Iso Propanone (IPA) and Benzoquinone (BQ).

The experiment 3 is the same with the experiment 1.1, except the participation of three solutions including KI, IPA and BQ played as the radical scavengers.

10.3 Data recorded



FIGURE 20. ZIF 67 product



FIGURE 21. The measurement of absorption level

Figure 20 shows the ZIF 67 created mixed with methanol solution before this mixture went to the centrifuge and heating to collect the crystal ZIF 67. The color of ZIF 67 is blue-purple solid.

Figure 21 the absorption level of congo red at the beginning was 0.688 under dark environment in 60 minutes. After that, when mixing the ZIF 67 as catalyst with congo red and the involvement of mercury light, the absorption level of congo red was 0.041 and 0.034 in 30 minutes and 60 minutes.



FIGURE 22. 2-hydroxyterephthalic acid under the light with 315 nm and compared to water.

The mixture 2-hydroxyterephthalic acid was under the 315 nm light, the solution was luminescent which are shown in figure 22 This phenomenon proves that the formation of free radicals existing in the solution. The right scene of figure 22 shows the difference between two solution under the light, water was not luminescent while the other did. This is because water did not create free radicals.

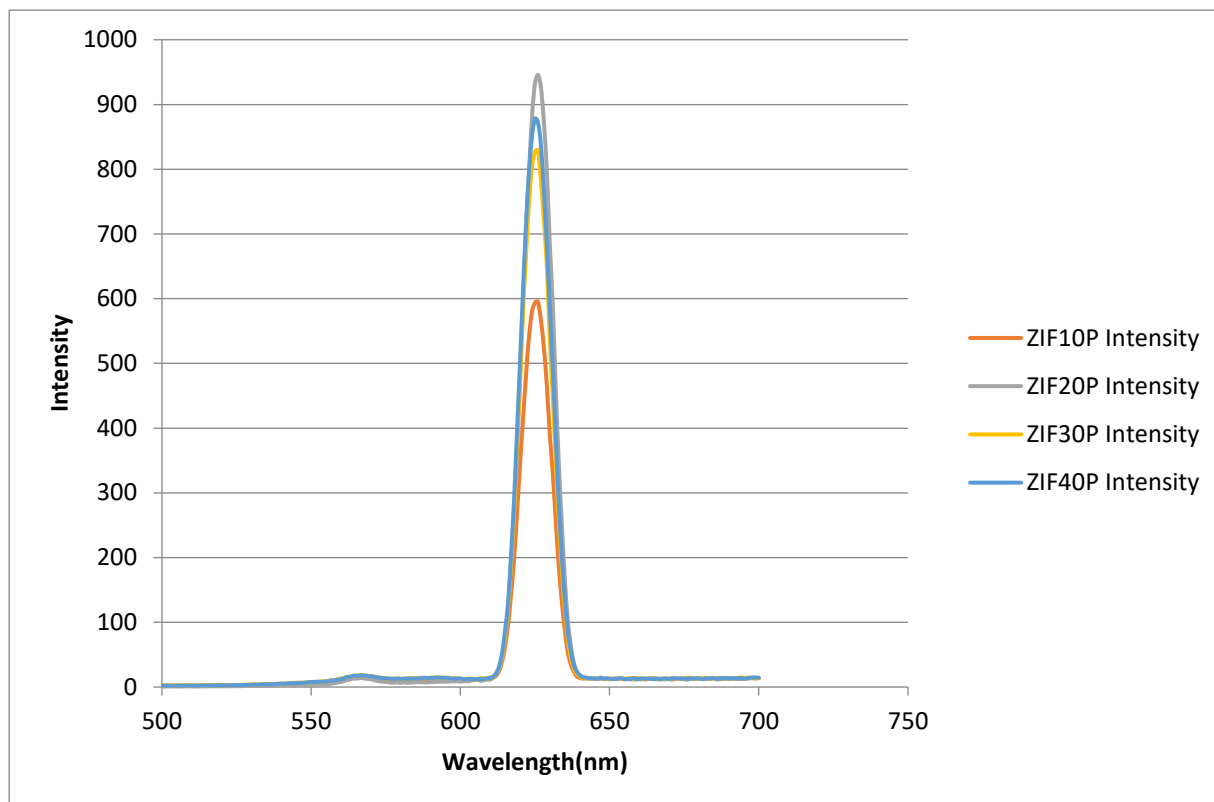


FIGURE 23. Fluorescence spectral changes observed during illumination of ZIF 67 in 4×10^{-4} M

Sodium hydroxide solution of terephthalic acid (excitation at 315 nm). Each fluorescence spectrum was recorded every 10 min of UV illumination.

According to the figure 23, at wavelength 625 nm, the intensity of fluorescence of free radicals reached a peak. After every 10, 20, 30 and 40 minutes, the level of intensity changed at the same wavelength.

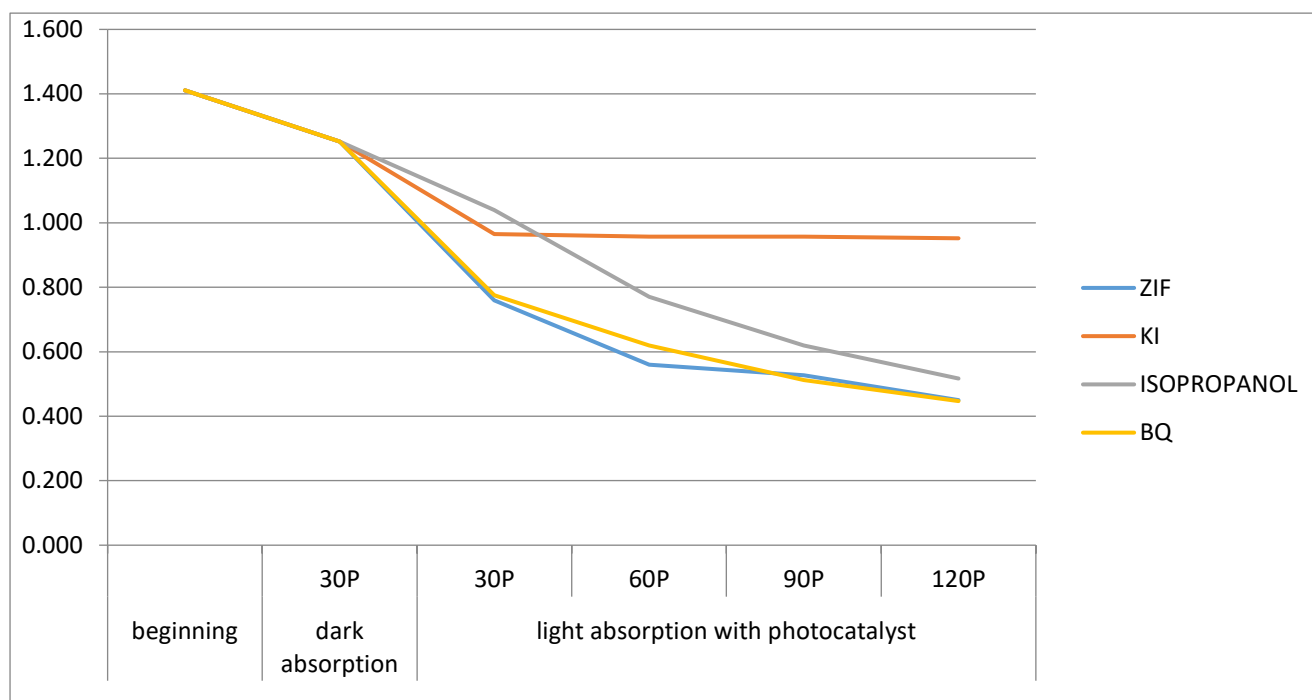


FIGURE 24. Congo red removal rates via ZIF 67 photocatalysis in the presence of KI (hole scavenger), isopropanol (hydroxyl radical scavenger), and benzoquinone (superoxide scavenger).

In this experiment, the role of each radical scavenger solutions is to determine the mechanism of each reaction and the free radicals which was performed in the destruction of dye. According to figure 24, the involvement of KI contributes the huge impact on the reaction because the concentration does not change in 120 minutes while the rest has the same downward tendency of concentration.

10.4 Evaluation of the experiments

In the experiment 1, the formation of ZIF 67 was successfully performed. Besides, the purpose of ZIF 67 is to destroy the dye color (congo red) was also achieved through the change of absorption level under the mercury light, the absorption level was decreased from 0.688 to 0.041 and 0.034.



FIGURE 25. The color 's change of Congo red.

Besides, the figure 25 demonstrates that the color of congo red was paly compared to the beginning. Turning to the experiment 2 is the determination of the fluorescence intensity of ZIF 67 when mixing with terephthalic acid at 315 nm. Figure 23 illustrates that the intensity level increased that lead to more free radicals are generated and got the peak at 625 nm with time but because the free radicals were weak and unstable. Therefore, the recombination of free radical is performed after long time.

When it comes to the last experiment, electron holes play a vital role in the destruction of dye color because when KI appeared in the solution, it kept the electron holes to participate in the reaction leading to the concentration of dye did not change.

11 CONCLUSIONS

In the final thesis, it is noticeable that the importance of MOFs and ZIFs into the industrial aspects such as the storage and separation of gas, sensing properties and photocatalysis. Especially, the ZIF 67 plays as the photocatalyst for dye destruction has been successfully achieved through the removal of congo red. The photocatalysis could be the main method of waste water treatment in the near future. Heterogeneous photocatalysis using semiconductors such as ZIF material can be more interesting than conventional method for destroy organic pollutant in wastewater. After the process, the original material will be collected to reuse and therefore no sludge requiring disposal landfill is produced. The catalyst did not consume in the reaction so they are unchanged and the phase of material is solid phase so it is really easy to collect by filtration method.

Besides, the understanding of mechanism of free radicals as well as their formation during the process was clearly displayed. The analysis of hydroxyl radical by using fluorescence technique under the ultraviolet light is successful. In the experiment the terephthalic acid react with hydroxyl radical produce 2-hydroxyterephthalic acid. According to our data, the result surprisingly showed that the peak free radical is appeared at 625 nm of wavelength while the peak of free radicals from other research was happened at 425 nm. During the congo red degradation under UV light, it is clearly to see that when the larger specific surface area and the greater the formation rate of $\bullet\text{OH}$, the enhanced of the photocatalytic activate and the increase of reaction rate. In the radical scavenging experiment, the results demonstrate that the potassium iodide did not affect to the degradation of congo red. But when the IPA and benzoquinone is added, the decrease of degradation rate is observed. These results indicate that the electron hole play an important role in the organic pollutant degradation.

Generally, the thesis is comprised of the necessary information about ZIFs materials as well as the photocatalysis process and its application for any industrial fields especially wastewater treatment. Photocatalyst have many benefits but however an idea of photocatalyst should be cost affordable, non-toxic, renewable, easy to perform and high effective.

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