



**PHOTOCATALYTIC DEGRADATION OF METHYLENE BLUE DYE FROM  
AQUEOUS SYSTEMS BY HKUST-1 and CuO@HKUST-1**

By

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## **DEDICATION**

This work is dedicated to my lovely parents and sisters who encouraged me throughout the course of this degree.

## **ACKNOWLEDGEMENTS**

My gratitude goes to my supervisor Dr G. Mehlana for his encouragement, guidance and inspiration throughout this research. I would also want to thank the Midlands State University laboratory staff. I would also want to thank my family and my friends for their love and support during this course. Above all I thank God for giving me the gift of life.

## **ABSTRACT**

High concentrations of methylene blue (MB) in aqueous environments have detrimental effects to both plants and animals and hence its removal is very important. Metal Organic Framework, HKUST-1 and composite, CuO@HKUST-1, were synthesized and characterised for their functional groups before and after degradation of methylene blue. Studies were done to optimize the degradation of methylene blue and to characterize the degradation system with respect to photocatalytic degradation kinetics. The optimum methylene blue degradation conditions were pH 4, catalyst dosage of 50 mg and contact time of 180 minutes for CuO@HKUST-1 and pH 6, catalyst dosage of 100 mg and contact time of 180 minutes for HKUST-1. The pseudo first order kinetics best described the data ( $R^2$  0.991 and 0.992 for HKUST-1 and CuO@HKUST-1 respectively). Methylene blue showed negligible self catalysis properties suggesting that it is very stable to light. CuO@HKUST-1 was found to have better photocatalytic degradation efficiency (95 %) as compared to HKUST-1 (75%). CuO@HKUST-1 proved to be an effective and stable catalyst which can be re used for 4 times producing a degradation efficiency of more than 80 %.

**DECLARATION**

I, **Fadzanai Fusirai**, hereby declare that I am the sole author of this dissertation. I authorize Midlands State University, Gweru, Zimbabwe to lend this dissertation to other institutions or individuals for the purpose of scholarly research.

Signature .....

Date .....

## **APPROVAL**

This dissertation entitled, '**Photocatalytic degradation of methylene blue dye from aqueous systems by HKUST-1 and CuO@HKUST-1**' by **Fadzanai Fusirai** meets the regulations governing the award of the degree of Chemical Technology of the Midlands State University and is approved for its contribution to knowledge and literal presentation.

Supervisor: .....

Date: .....

## LIST OF ABBRIVIATIONS

MOF	Metal Organic Frameworks
CuO NPs	Copper Oxide nanoparticles
FTIR	Fourier Transform Infra-Red Spectroscopy
BTC	benzene-1,3,5-tricarboxylic acid
MB	Methylene Blue
SEM	Scanning electron microscope
KBr	Potassium bromide
TGA	Thermal Gravimetric Analyzer
UV-Vis	Ultra Violet-Visible Spectroscopy
ppm	parts per million
m g	milligrams
m g /L	milligrams per litres
mL	millilitres

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## **CHAPTER 1**

### **1.0 INTRODUCTION**

This chapter briefly gives a background of the project and also outlines the aims and objectives to be met. It describes the problems associated with pollution of water by methylene blue dye and other methods which have been used for treatment. A justification for the use of photocatalysis by metal organic frameworks as a method of degrading methylene blue is also given.

### **1.1 BACKGROUND**

In the past years environmental pollution has resulted in critical social challenges in the human society. Waste water has been found to contain dyes from different industries, polluting water. When in excess, dyes are potentially risky to the human health. The production of these dyes and pigments is more than 7 (10<sup>5</sup>) tons and approximately 5 to 15 % is lost in the industrial effluents [1]. The dyeing and finishing processes in textile industries are the major sources of pollution. It is not easy to remove dyes from waste water owing to their stability to oxidizing agents, they also undergo slow or incomplete degradation process hence generates some environmental problems [2].

Once organic contaminants are released into the aquatic ecosystem they can generate numerous environmental problems such as depressing light penetration, affecting photosynthesis and adversely affecting aquatic biota [3]. There are various organic pollutants; these include methylene blue dye, a cationic dye mostly used in paper, rubber and textile industry as a colorant. Deep coloured methylene blue (MB) dye is discharged widely in wastewater and the existence of MB in water can cause irritation on eye, nausea, vomiting and diarrhoea when in contact or when taken orally by humans [4].

Physical, chemical and biological methods are being used to remove organic dyes and pigments from waste water. However, the traditional methods such as adsorption, coagulation and membrane separation have been found to be too expensive and also generate a secondary pollution problem. Among other methods, advanced oxidative processes (AOPs) which include ozonation, Fenton reaction and photocatalysis, have been used in the destruction of organic contaminants [5]. Photo catalytic degradation (combination of a semi conductor and UV light) method is being given more attention because of its efficiency, versatility, convenience, ease of process, low cost, environmentally clean process for treatment of pollutants. Another advantage of photocatalysis is its ability to break down the pollutants into less toxic compounds such as  $\text{CO}_2$  and  $\text{H}_2\text{O}$  [6].

Heterogeneous photocatalysis using various metal oxides and semi conductor catalysts ( $\text{ZnO}$ ,  $\text{CdS}$ ,  $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{ZnS}$ ) and related compounds came out as highly efficient technique to overcome the problems. With heterogeneous photocatalysis, there is complete mineralization of intermediate compounds hence this reduces risk of secondary pollution and it also has lower operating costs. However their efficiency is still low due to other reasons including wide band gap, recombination of electron hole pairs, problems in post separation and easy agglomeration [2].

To date, large variety of traditional heterogeneous photocatalyst such as transition metal oxides semiconductors (such as  $\text{TiO}_2$ ) and including their hybrids with noble metals, quantum dots, non-metal doped semiconductors, carbon nanotubes and graphene derivatives have been used for the photodegradation of MB in effluents under UV and visible light irradiation [7]. However, in the above studies, a number of limitations have been noted hence the degradation process has not been efficient. Need of the day is to find new class of low cost photocatalyst which show high efficiency, high rate constant, enhanced absorption of

irradiated light, improved photocatalytic properties hence an improvement in the dye degradation.

A new class of hybrid inorganic – organic porous material, metal organic frameworks (MOFs), due to their structures, have been found to have various applications, one of them being catalysis [8]. MOFs have organic linkers which connect metal containing nodes through strong chemical bonds. Some MOFs act as semiconductors when exposed to light hence they are potential photocatalysts [9].

In this particular study attention has been given to the use of metal oxides and metal organic frameworks for the degradation of methylene blue. MOFs have regular pores, high surface area and channels which provide the required interaction between substrates and reaction sites thus allowing efficient catalysis. MOFs do not only act as photocatalysts but they can be used for embedding metals or metal oxides into their porous structure thus acting as a sacrificial template and improving the whole photocatalysis process [5].

## **1.2 AIM**

To compare the photocatalytic degradation of methylene blue dye using HKUST-1 and CuO@HKUST-1 under sunlight irradiation.

## **1.3 OBJECTIVES**

- To synthesize HKUST-1 and CuO@HKUST-1
- To characterize using FTIR, TGA, SEM and XRD
- To optimize pH, catalyst dosage and contact time during degradation by HKUST-1 and CuO@HKUST-1
- To determine the effect of initial methylene blue concentration on the degradation of MB by HKUST-1 and CuO@HKUST-1
- To determine the re-usability and stability of CuO@HKUST-1 during degradation of MB

## 1.4 PROBLEM STATEMENT

The release of coloured dyes into the environment has been of great concern of late due to the properties and effects of dye contaminated water to the environment. Apart from having high stability to temperature, water, detergents, chemicals and light, dye contaminated water has a high biological oxygen demand (BOD) and high chemical oxygen demand (COD) as well [10]. Dye contaminated waste water disposal is of concern because it is toxic to the humans and aquatic life. These dyes are not biodegradable and cause water pollution and serious long term effects to the environment. Dyes are carcinogenic, mutagenic and toxic to life. Quality and transparency of water bodies is affected even by the small amounts of dyes present in the water bodies [4].

This leads to the destruction of aquatic life because these dyes decrease light penetration, thus decreasing photosynthetic activity, this will result in oxygen deficiency. Beneficial uses of water usually done downstream such as drinking water, irrigation and recreation are limited. In cases where there is ingestion by humans, this can cause DNA damage as a result of metabolism by intestinal micro organisms [11]. Other methods like adsorption by activated charcoal have been found to be effective; however, they result in large amounts of sludge which will cause pollution problems again. Methods of removal of these dyes which have been employed cause toxic sludge and disposal problems [4].

Photocatalysis has proven to be a more efficient method of degradation of methylene blue, however, some of the photocatalysts being employed have shown a number of draw backs which include the recombination of the photogenerated electrons and electron holes thus reducing the rate of degradation [6]. Other problems associated with the use of these semiconductors is a large band gap which will require more energy before electrons are excited from the conduction band to the valence band. These problems can be addressed by the use of metal organic frameworks and their composites [12].

## 1.5 JUSTIFICATION

Dyes which are being continuously released by industries into the environment have been of great concern lately. Photocatalytic degradation is a clean purification method for wastewater [11]. Unlike other old purification methods where the reaction is very slow and pollutants are separated or transferred to another phase producing large amounts of sludge, photocatalytic degradation directly converts pollutants to less toxic products under light irradiation. There is no formation of secondary hazardous products while using very cheap and active catalysts [13]. Photocatalytic degradation using metal oxide semiconductors becomes inefficient where there is a large band gap hence only a certain percentage will absorb light resulting in less degradation of the pollutants. However copper oxide nanoparticles have a lower band gap of 1.2 eV. It requires less activation energy to produce highly reactive radicals such as  $\text{OH}^-$  to destroy pollutants; it can be activated in visible light near sunlight [14].

HKUST-1 MOF has an intrinsically high surface area and regular pores and channels that allow efficient interaction between substrates and reaction sites, beneficial to the overall catalytic performance [15]. It has a large surface area and higher adsorption capacity in comparison to other conventional semi conductors and adsorbents. HKUST-1 has better hydrothermal stability which makes it makes it suitable to couple with CuO nanoparticles [16].

Therefore, loading CuO nanoparticles into the pores of HKUST-1 will increase the number of active sites thus improving the light absorption ability hence increasing the number of active sites to promote the separation of electron and hole pairs. Electron recombination is also reduced by coupling the nanoparticles and MOF together thus enhancing degradation of methylene blue under visible light irradiation [17].



## CHAPTER 2

### LITERATURE REVIEW

#### 2.0 Introduction

This chapter mainly focuses on the degradation of MB from aqueous systems by the use of synthesized HKUST-1 and CuO@HKUST-1. It outlines the different sources of dye waste water, the impact of dyes in humans and the environment and the various conventional methods for dye removal. The use of metal oxide nanoparticles, metal organic frameworks and their composites are also explained in this chapter, with specific interest being given to copper oxide nanoparticles and copper based MOF HKUST-1.

#### 2.1 Dyes

These are synthetic or natural substances that are used to add colour. They have affinity to the substrate to which it is applied. Dyes can be natural (derived from plant sources) or synthetic (man-made). Most dyes are organic compounds, however unlike most organic compounds, dyes possess colour [18]. This is because they absorb colour in the visible range, they have colour bearing groups (chromophores), they consist of a resonance of electrons and they also have a conjugated system. Methylene blue dye is an aniline based dye usually used in the textile industry. It occurs in the form of several different hydrates. It is a cationic dye that releases aromatic amines and a potential carcinogen [19].

##### 2.1.2 Sources of water polluting dyes

Dyes are primarily used in the production of consumer products; this includes paper, textile, paint, printing inks and paper. These dyes are discharged either in process waste waters, maintenance waste waters or as a result of degraded, rejected or expired dye containing products improperly disposed. These dyes end up accumulating in water bodies and

disturbing some environmental processes taking place thus affecting plants, animals as well as human beings. [18]

### 2.1.3 Structure and uses of methylene blue

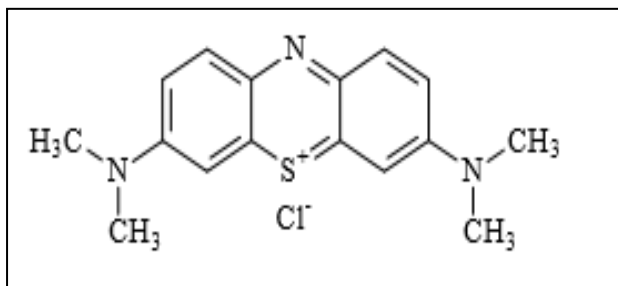


Fig 2.1 structure of methylene blue

Methylene blue, shown in Fig 1, has a relative molecular mass of 319.85, in its anhydrous form. At room temperature it is a solid, odourless, dark green powder that yields a blue solution when dissolved in water. Its melting point is between 100 and 110 degrees Celsius and has a density of 1.0 g/m L at 20 °C. Its solubility is 43.6 g/L in water; it is soluble in ethanol as well [20].

Methylene blue's production and use as a paper dye, microscopy stain, chemical intermediate, medicinal agent, and cosmetic dye may result in its release to the environment through various waste streams. The trihydrate of methylene blue has UV absorption maxima at 663 nm and therefore methylene blue may be susceptible to direct photolysis by sunlight [21]. Methylene blue is a cationic stain and exists in the ionic form at pH values of 5 to 9. Hydrolysis is not expected to be an important environmental fate process since this compound lacks functional groups that hydrolyze under environmental conditions [22].

However, methylene blue has been classified as having good "fastness" properties with respect to light which means that it is resistant to destruction by sunlight. Its IUPAC name is 3,7-bis(Dimethylamino)-phenothiazin - 5 -ium chloride [20].

Methylene blue can be used as

- A redox indicator in analytical chemistry
- A peroxide generator
- A biological stain
- used as a colorant on paper, leather, clothes
- a temporary hair colorant

#### **2.1.4 Effects of methylene blue on humans and environment**

MB, although not considered to be a very toxic dye it can reveal very harmful effects on the living things. After being inhaled, symptoms such as difficulties in breathing, vomiting, diarrhoea and nausea can occur in humans. When excess methylene blue dye comes in contact with humans, it may result in dizziness, headache and upset stomach. Chest pain and confusion are serious long term effects of MB to humans. Dyes are carcinogenic, mutagenic and toxic to life [23].

To the environment, quality and transparency of water bodies is affected even by the small amounts of dyes present in the water bodies. This leads to the destruction of aquatic life because these dyes decrease light penetration, thus decreasing photosynthetic activity, this will result in oxygen deficiency [9].

#### **2.2 Methods of removal of methylene blue**

Different treatment methods have been used for the removal of methylene blue dye from waste water. The 3 main classes of treatment methods are physical, biological and chemical methods [18].

##### **2.2.1 Physical treatment methods**

Removal of dyes by physical methods includes adsorption and ion exchange.

The processes are influenced by a number of factors such as temperature, particle size and pH. Adsorption has been mostly used where the sorbent is cheap and readily available, activated carbon is the most common one and it has been used because of its higher adsorption capacity. In adsorption the dyes are only transferred from aqueous solution onto the sorbent material, thus creating secondary pollution problems [24]. Ion exchange has not been widely used due to its limitations which include that it cannot accommodate a wide range of dyes. Filtration and coagulation / flocculation can also be employed as part of the physical treatment methods [20].

### **2.2.2 Biological treatment methods**

This includes use of processes such as aerobic and anaerobic degradation; this involves use of a suitable fungi, algae or bacteria for either bio absorption or degradation of the dyes in water. The fungi, being extracellular in nature, have the advantage of being able to tolerate very high concentrations of dyes. These methods are also affected by factors such as pH and contact time, as in the physical treatment methods [25].

### **2.2.3 Chemical treatment methods**

These include the Fenton reagent technique, ozonisation and photocatalytic methods. These methods fall under some advanced oxidation processes (AOPs) [23] which focuses on complete oxidation of organic compounds to products which are not harmful like carbon dioxide and water. AOPs can be divided into two groups

- i) Non photochemical AOPs – these include wet air oxidation, ozone/hydrogen peroxide, ozonation, cavitations and Fenton and Fenton like processes.
- ii) Photochemical AOPs – these photocatalysis processes. The purpose of AOPs is to produce hydroxyl free radical ( $\text{OH}^\cdot$ ) and use them as strong oxidants that will destroy compounds that cannot be oxidized by the conventional oxidant [21].

## Basic principles of AOPs

- Light falls on the surface of the semiconductor catalyst
- Valence band electrons are excited and move to the conduction band
- Holes are left in the valence band and these will react with water to produce hydroxyl radicals
- The oxidative reaction between the radicals and the organic pollutants takes place, producing biodegradable intermediates
- The oxidants react with the biodegradable intermediates in a process called mineralization; this produces water, carbon dioxide and other inorganic ions [26].

### 2.3 Photocatalysis

Amongst other advanced oxidation processes, photocatalytic degradation using semiconductors has been considered to be most effective. It is a combination of photochemistry and catalysis [27]. In this technique, the semiconductor is used as a catalyst which will be acting as a medium of oxidation. An ideal photocatalyst should be inexpensive, non-toxic, highly photoactive and stable in the conditions in which the pollutant is present. Photocatalysis can be divided into two classes homogenous and heterogeneous [6].

#### 2.3.1 Main advantages of photocatalysis

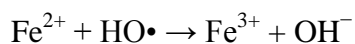
- i) It does not transfer pollutants from one phase to another like in other conventional treatment methods. It results in the production of harmless products
- i) Less chemical input is required
- ii) There is less secondary waste generation
- iii) Can be applied in all phases (gaseous, aqueous, solid)
- iv) Uses solar energy which is renewable and pollution free [16].

#### 2.3.2 Limitations of photocatalysis

- i) Requires improved charge separation
- ii) Charge carrier recombination can affect the process

### 2.3.3 Homogenous photocatalysis

The reactants and photocatalysts exist in the same phase, common homogenous photocatalysts are ozone and photo Fenton systems, and these are most efficient at lower pH levels because at higher pH the iron will precipitate [28]. The iron will also have to be removed after the treatment which is one of the major disadvantages. Hydroxyl ions are produced and act as the reactive species. The concentration of hydrogen peroxide and UV light intensity are also some of the parameters which control the Fenton type reaction [29]. The main advantage is that it can use light of about 450nm thus it can make use of sunlight thus a cost effective method. Mechanism for production of hydroxyl ion in Fenton process is shown below



### 2.3.4 Heterogeneous photocatalysis

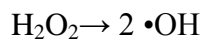
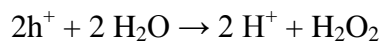
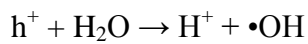
The catalyst and reactants are in different phases. The most commonly used photocatalysts are transition metal oxides and sulphides as semiconductors. Semiconductors possess a gap in between the two bands, valence band and conduction band, and this is called the band gap energy [5]. The semiconductor comprises of a filled valence band and an empty conduction band. When light falls on the semiconductor, the energy must be equal enough to excite an electron from the filled valence band and promotes it to the empty conduction band. The valence band is left with positive valence band holes, and excited state conduction band will have electrons [12].

Charge carriers in the resultant holes and electrons may undergo some processes which include;

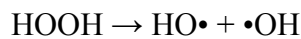
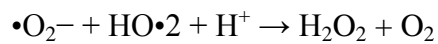
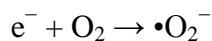
- i) They can recombine and release of input energy as heat
- ii) They can get trapped into the surface of the catalyst
- iii) Recombination of the trapped charge carriers
- iv) Electron donors or acceptors adsorbed on the surface of the semiconductor can also carriers react [13].

The goal of the design of photocatalysis is to facilitate reactions to take place between

- a) Generated holes react with reductants to produced oxidized products (oxidative reactions)



- b) Excited electrons react with oxidants to produce reduced products (reductive reactions)



## 2.4 Semiconductor photocatalysts

Photocatalysts are activated by photons of appropriate energy and change the rate of a chemical reaction without being involved in a chemical transformation. Semiconductors have an energy band (band gap) between the filled valence band and the lower unoccupied conduction band [30]. Their light absorption properties and electronic structures make them

useful as photocatalysts. Transition metal oxides are the most common semiconductor photocatalyst however metal organic frameworks can also be used as a semiconductor photocatalyst in contact with a liquid during heterogeneous photocatalysis [31].

#### **2.4.1 Copper oxide nanoparticles**

Researchers have been focusing on the reactions that take place on the surface of semiconductors such as metal oxides, sulphides, and selenides [13]. These have average band gap energy of between 1.1 to 3.8 eV. Nanoparticles have been in use for degradation of several types of dyes; with the common one being titanium oxide and other metal oxides because metal sulphides and selenides are not stable, corrosive as well as photo anodic corrosive [17].  $\text{TiO}_2$  been successfully employed as the major catalyst for photocatalytic degradation, however, owing to its large band gap and a number of other draw backs, other metal oxide nanoparticles have been introduced. In this research copper oxide nanoparticles are of interest [32].

CuO NPs have been prepared with different shapes and sizes using different methods which include sonochemical, direct decomposition, microwave radiation. In this particular research CuO NPs have been prepared using a simple chemical precipitation method [33]/ Copper is a one of the mostly used materials in industries and has great significance in the various applications. It has attracted attention in photocatalysis due to its unique properties.

Copper oxide is a p type conductor with a narrow bad gap of 1.2 e V; it makes use of the hydroxyl radical production under visible light [34].



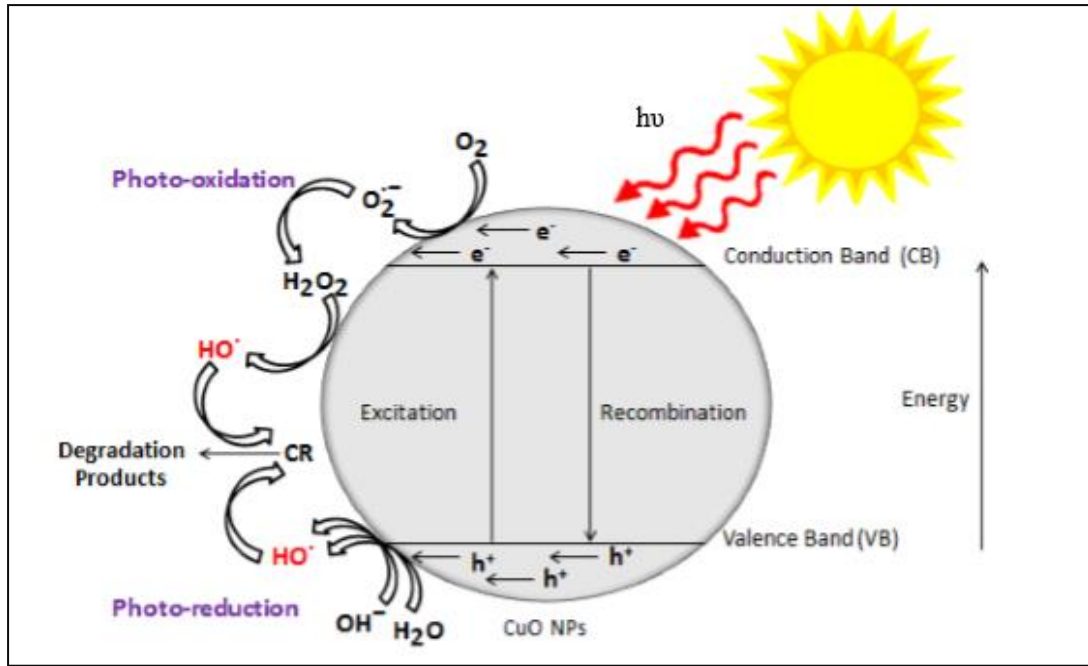
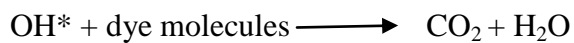
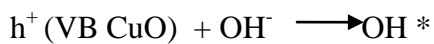
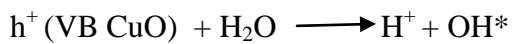
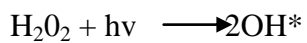
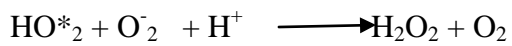
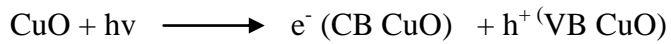


Fig 2.2 Photocatalysis mechanism using CuO NPs

The mechanism of degradation of pollutants by CuO NPs has been shown in fig 2.2 and the chemical equations associated with the mechanism are as follows;



The semiconductor nanoparticles, CuO, absorbs light of energy equal or higher than its band gap energy, this results in an electron being excited from the valence band to the conduction band. In the photo-excitation stage, a vacancy is created at the valence band,  $h^+$ , the  $e^-$  represents the excited electron at the conduction band. A pair of electrons ( $e^-$ ) and hole ( $h^+$ ) is generated [13]. The vacancies (holes) react with water to form hydroxyl radicals ( $OH\cdot$ ). At the same time, electrons react with oxygen to form a series of oxidizing species like superoxide anion, hydrogen peroxide and hydroxyl radicals. The cycle will continue in the presence of light. This is a heterogeneous photocatalysis process whose photocatalytic activity is as a result of photo-induced electrons and corresponding positive holes formed [11].

In this research, semiconductors (CuO NPs) were encapsulated into metal organic frameworks for effective degradation process. These MOFs have been found to have very large surface areas as well as high specific pore volumes.

#### **2.4.2 Metal organic frameworks**

MOFs are porous hybrid compounds constituted by organic molecules and metal ions linked together to form crystalline networks with high surface area and large pore volume [16]. They have been recently reported for their application in the field of photocatalysis. Reports have highlighted that MOFs have shown good photocatalytic properties and photocatalytic activity owing to their fascinating structure properties. MOFs are synthesized through reaction of organic linkers and inorganic metal in the presence the required solvent, temperature and pressure [35].

It is reported that MOFs have unique properties that make them excellent candidates for many applications. They are very porous material with high surface area thus making them good material for catalytic purposes [36]. When the right MOFs are carbonized, metal/metal

oxide nanoparticles will be encapsulated in highly porous matrices resulting from the original organic ligands. Therefore, the original MOF will not only provide the carbon sources but also act as sacrificial templates. The final hybrid composites can also be utilized for various photocatalytic applications [9].

The structure that results has a very micro porous crystalline framework and other properties that make them fit for a wide range of applications. Integrating metal organic frameworks, having properties like good gas adsorption, with photocatalytic material like copper oxide promotes photogenerated electron transfer thus enhancing photocatalytic activity. MOFs have high specific surface areas and various chemical functionalities which make them suitable for areas like photocatalysis [8].

One of the most promising (MOF) and of interest in this research is HKUST 1 with a chemical formula,  $\text{Cu}_3(\text{BTC})_2(\text{H}_2\text{O})_3$ , prepared by combining a benzene tricarboxylic acid, H3BTC and  $\text{Cu}^{2+}$  ions forming a complex array of metal organic complex. It portrays resistance in the presence of both water and air [15]. It works well as catalyst because of its metal sites which are strongly active in a number of reactions; these are also easily accessible by a number of molecules due its surface of large pores. However, at certain conditions MOFs are unstable making them unsuitable as efficient catalysts; as a result, nanoparticles have been used to enhance catalytic activity as well as recyclability of the catalysts [22].

The metallic group of HKUST-1 involves a pair of  $\text{Cu}^{2+}$  ions (each with electron spin  $S=1/2$ ) coordinated by four carboxylate bridges to form a paddle-wheel moiety; each carboxylate group is part of a benzene 1,3,5-tricarboxylate (BTC) linker molecule (Figure 1).5,9 In the as synthesized HKUST-1, the fifth (out of plane) binding site on each  $\text{Cu}^{2+}$  ion is occupied by the oxygen of a crystallization water molecule which can be easily removed by the activation process [16].

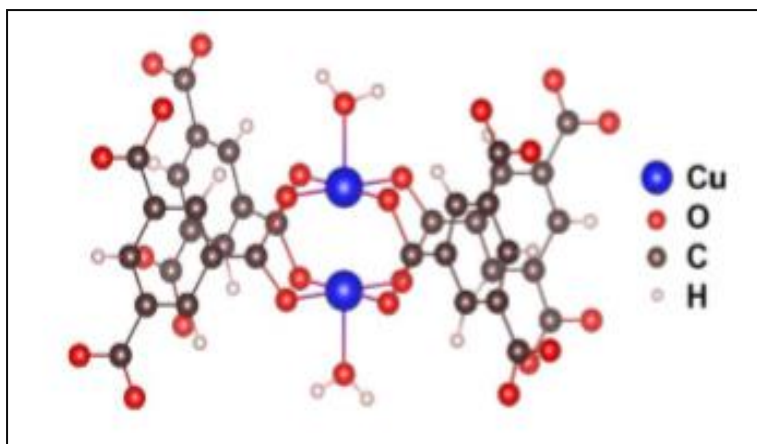


Fig 2.3 Structure of HKUST-1

The porous structure of HKUST-1 is shown in Fig 2.3, its porosity allows it to work as a host for metal oxide nanoparticles and HKUST-1 can provide an especial pathway for photogenerated electrons migration and thus restrain the recombination of electrons and holes to increase the photocatalytic efficiency [35].

#### 2.4.3 CuO@HKUST-1 as a photocatalyst

This composite system of a mixture of a metal oxide (CuO NP) and metal organic framework (HKUST-1) reduces the band gap and this enables the composite catalyst to absorb in the visible range and thus achieving higher photocatalytic activity [31]. Each of the catalyst in the composite system has its own energy level system so this helps in accomplishing charge separation. The conduction band for CuO (1.2 eV) is lower than that for HKUST-1 (3.5 eV) therefore the former will act as a sink for photogenerated electrons as illustrated in Fig 2.4. Holes move in the opposite direction with electrons therefore the photogenerated holes in HKUST-1 will be caught up within itself, thus accomplishing charge separation resulting in an increase in degradation efficiency [37].

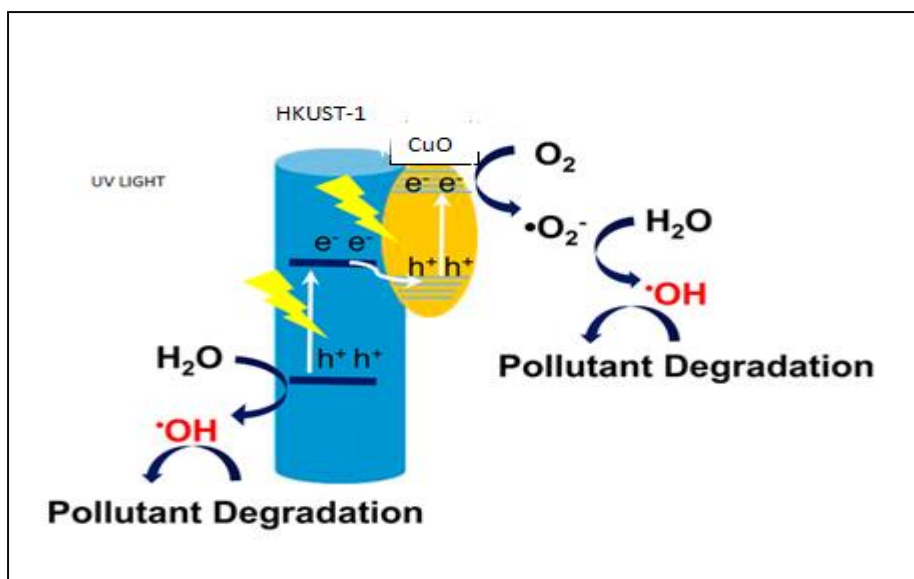


Fig 2.4 Photocatalysis mechanism using CuO@HKUST-1

## 2.5 Operating and affecting parameters of photocatalysis

The efficiency of photocatalytic system and oxidation rates depends on a number of factors. These operational parameters govern the photodegradation of the organic molecule. Several researchers have reported the significance of these parameters [38].

### 2.5.1 Crystal structure, shape, size and surface area of semiconductor

The morphology and structure of the photocatalyst is important to the photocatalysis process, this is because there is a direct relationship between organic compounds and surface coverage of the photocatalyst [10]. Nanoparticles and metal organic frameworks have larger surface area thus they possess a higher number of active sites for photocatalysis, there will be an increase in the surface to volume ratio. Photocatalysis also takes place on the absorbed phase of the photocatalyst therefore the surface properties of the semiconductor are very important [12].

### 2.5.2 Effect of pH

The pH of the solutions affects the electrostatic interactions between the contaminants and the charged particles. Therefore the pH of solution is important as it interferes with the surface charge properties of the photocatalyst; it therefore shifts the potentials catalytic reactions. For most photocatalysts excess  $H^+$  and  $OH^-$  have been found to decrease the reaction rate [39].

### **2.5.3 Effect of amount of catalyst**

As the amount of catalyst increases there will be an increase in the number of active sites, thus an increase in the production of the hydroxyls and superoxide species responsible for degrading the pollutant. With an increase in the amount of catalyst there is an increase in the degradation rate, which is a feature of heterogeneous photocatalysis. There is an increase up to an optimum point where the amount of catalyst will disturb the passage of light into the solution [14].

### **2.5.4 Effect of initial concentration of dye in the solution**

Because photocatalysis is mainly dependent on the passage of light through the solution, the degradation will decrease with an increase in dye concentration. It will also affect the irradiation time required for the degradation to attain complete mineralization. Previous reports have shown that the rate of degradation is inversely proportional to the initial concentration of the pollutant [38].

### **2.5.5 Dissolved oxygen**

Dissolved oxygen in photocatalysis acts as an electron acceptor, it traps the excited electrons released from the conduction band. This prevents the electron – hole recombination thus ensuring a smooth photocatalysis reaction. The trapping of electrons by oxygen also forms super oxide ions which also directly attacks the pollutants for degradation [38]. Cleavage mechanism for aromatic rings in organic pollutants is also induced by the presence of

dissolved oxygen. Continuous stirring in open air during photocatalysis aids dissolving oxygen into the solution [26].

## CHAPTER 3

### METHODOLOGY

#### 3.0 Introduction

The chapter presents, chemicals, equipments, synthetic routes and characterisation techniques used in this study. The synthesis of CuO nanoparticles using chemical precipitation method, synthesis of HKUST-1 and the method of encapsulation of CuO NPs into HKUST-1 to form CuO@HKUST are outlined in this chapter. The application of synthesized composites towards photocatalytic degradation of methylene blue is also described.

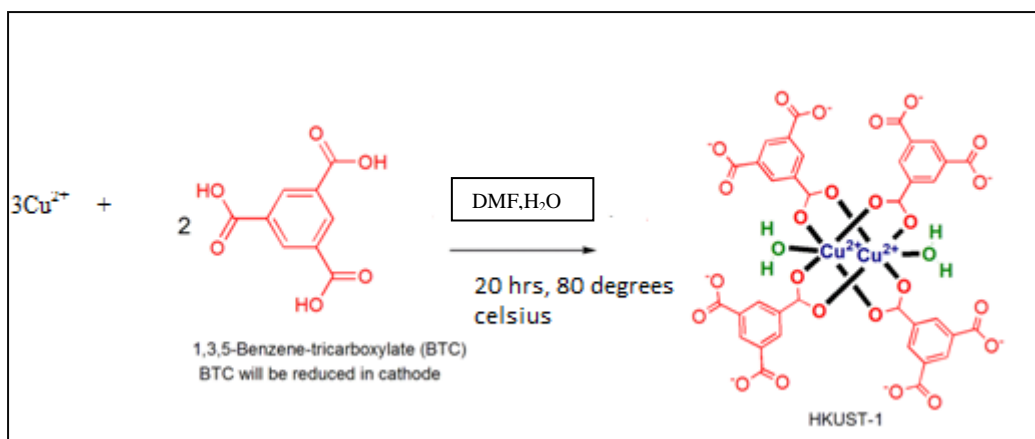
#### 3.1 Reagents and instrumentation

All the chemicals that were used in this investigation were of analytical reagent grade. Their masses or concentrations and the details of their suppliers are listed in Table A1 in Appendix A. The instruments that were used for the successful synthesis of CuO NPs, HKUST-1 and CuO@HKUST-1, its characterization and application to the degradation of MB studies are listed in Table A2 in Appendix A.

#### 3.2 Synthesis of HKUST-1

The synthesis of HKUST -1 was done according to a reported procedure with few changes.  $(\text{CuNO}_3)_2 \cdot 3 \text{H}_2\text{O}$  (0.87 g; 3.6 mmol) was dissolved in 10 mL of double distilled water in a vial. In a separate vial, BTC (0.22 g; 1 mmol) was dissolved in 10 mL of DMF. The  $(\text{CuNO}_3)_2 \cdot 3\text{H}_2\text{O}$  solution was quickly added in to the vial in which the BTC solution was contained. After continuous stirring for 10 minutes at room temperature, the vial was sealed with PTFE tape. The vial was then placed in an oven at 80 °C for 20 hrs to allow the mixture to react. After allowing the product to cool to room temperature the crystalline solid were collected and washed with  $\text{H}_2\text{O}$  and DMF [16]. Scheme 1 illustrates the scheme for the synthesis of HKUST-1.





Scheme 1: synthesis of HKUST -1

### 3.3 Synthesis of CuO nanoparticles

To synthesize CuO NPs via chemical precipitation method, a standard procedure was followed. During synthesis of CuO NPs, 9.0 g copper (ii) chloride dehydrate and 5.4 g of sodium hydroxide pellets were dissolved in 25 mL and 75 mL of ethanol respectively. Drop wise addition of sodium hydroxide solution to copper (ii) dehydrate solution was carried out with constant stirring at room temperature. The colour of the solution turned was turned from green to bluish green and finally black as the reaction proceeded. The black precipitate was centrifuged then washed with ethanol and deionised water to remove sodium chloride salt solution. The precipitate was dried at 50 °C in the oven. The dried sample was annealed 600 °C to obtain crystalline CuO NPs [34]. The reaction that takes during the synthesis of CuO @HKUST-1 is given below



### 3.4 Synthesis of CuO@HKUST-1

For the synthesis of CuO@HKUST-1, 0.932 g of Cu (NO<sub>3</sub>)<sub>2</sub> 3H<sub>2</sub>O (3.87 mmol) and 0.258 g of CuO NPs were dissolved in 25 mL of ethanol at 60 °C. A solution of 0.491 g of BTC

(2.34 mmol) in 25 mL of DMF was added under stirring and the reaction mixture was refluxed for 24 h at 85 °C. The samples was the dried at 60 °C [31].

### **3.5 Characterisation of synthesized material**

The synthesized HKUST-1 and CuO@HKUST-1 were characterized using FTIR for identification of MB. The re used CuO@HKUST-1 was also characterized using FTIR.

#### **3.5.1 Characterisation using FTIR**

CuO NPs, HKUST-1, CuO@HKUST-1 were characterised using FTIR to establish the functional groups present. They were mixed with KBr in the ratio 1: 100 and ground to a fine powder, the powder was dried in oven and then used to make a disc and analysed in the FTIR spectrometer.

### **3.6 Photocatalytic degradation studies**

In photocatalytic experiments, MB dye (50 mL) and the catalyst CuO@HKUST-1 and HKUST-1, were placed in a beaker and exposed to sunlight for up to 180 min under continuous stirring. Dye samples of about 5 mL were taken out at a regular interval from the test solution, centrifuged for 4 min at 950–1000 rpm and their absorbance was recorded between 400 to 800 nm using a spectrophotometer. MB dye of concentration 20 ppm was prepared by dissolving 20 mg of MB in 1000 mL of distilled water [26].

#### **3.6.1 Examination of pH on dye degradation**

The efficiency of HKUST-1 and CuO@HKUST-1 in MB degradation was investigated in the 2 - 10 pH range at constant volume of 50 mL of 20 mg L<sup>-1</sup> MB solution and 25 mg catalyst (HKUST-1 and CuO@HKUST-1). The concentrations of initial MB solution and catalyst dosage were kept constant in aqueous solution whilst the solution pH was adjusted to the desired values by addition of dilute 0.01M hydrochloric acid and 0.01M sodium hydroxide [26].

### **3.6.2 Examination of catalyst dosage effect on dye degradation**

Different masses ranging from 10 mg to 200 mg of catalyst (HKUST-1 and CuO@HKUST-1) were added to a constant volume of 50 mL (20 mg/L) of MB solution in a set of labelled beakers. The beakers were exposed to sunlight while being magnetically stirred to ensure sufficient solid-liquid contact. After reaching the desired time interval, the suspensions with the different (HKUST-1 and CuO@HKUST-1) masses will be measured for level of dye degradation [40].

### **3.6.3 Examination of contact time**

The dye degradation efficiency by HKUST-1 and CuO@HKUST-1 as a function of time was examined by varying the suspension contact time over the range of 1-240 minutes using constant volumes (50 mL) of 20 mg/L initial concentration and 25 mg/L dosage. From each sample, 5 mL were taken for analysis using the UV VIS, after every 30 minutes [26].

### **3.6.4 Examination of initial dye concentration**

The effect of initial dye concentration on degradation by HKUST-1 and CuO@HKUST-1 was determined by adding 50 mL solutions of varying initial dye concentrations over the range of 10-40 mg/L. Samples were magnetically stirred under UV light for 180 minutes and examined for the level of degradation [41].

### **3.6.5 Determination of degradation capability of HKUST-1 and CuO@HKUST-1 at optimum conditions**

The optimised conditions of contact time, amount of catalyst, pH and initial dye concentration were used to carry out the comparative photocatalytic degradation of MB using CuO@HKUST-1 and HKUST-1 respectively [16]. The level of degradation was examined and the results used to calculate the percentage degradation of MB.

### **3.6.6 Determination of CuO@HKUST-1 adsorption capability and MB stability to light**

50 mL of 20 mg / L of methylene blue were added to 3 beakers and pH was optimised. To beaker A, 50 mg of CuO@HKUST-1 was added and exposed to sunlight under continuous stirring for 180 minutes. To beaker B, 50 mg of CuO@HKUST-1 was added and was continuously stirred in darkness for 180 minutes [42]. To beaker C, MB solution was continuously stirred under sunlight irradiation for 180 minutes without adding catalyst. Samples were then examined for absorbance using the UV-VIS.

### **3.7.7 Determining catalyst re-usability**

To 50 mL of 20 ppm MB solution at optimum pH, 50 mg of CuO@HKUST-1 was added and solution was continuously stirred for 180 minutes [42]. After 180 minutes, the solution was left to settle and then siphoned out for analysis using the UV-VIS. To the remaining solid (catalyst), a fresh solution of MB was added for degradation. Process was repeated until the catalyst was used for 4 times.

## CHAPTER 4

### RESULTS AND DISCUSSION

#### 4.0 Introduction

The section is focused on presentation of experimental findings and their discussion in comparison to the information from literature. The results are presented in various forms including graphs and tables.

#### 4.1 Characterisation of synthesized compounds

Identification of functional groups in the synthesized compounds using for identification of functional groups in the synthesized compounds

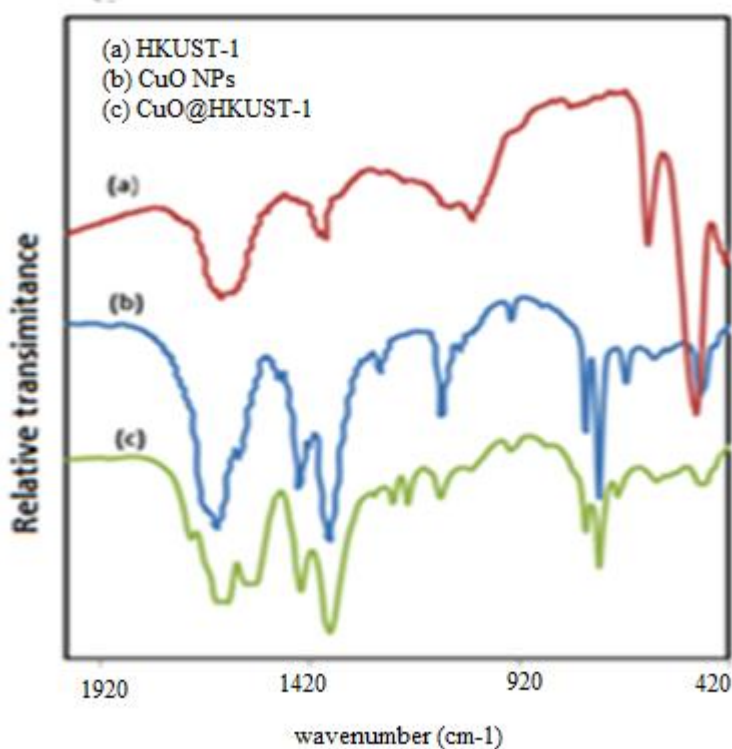


Fig4.1 FTIR spectra for HKUST-1, CuO NPS, CuO@HKUST-1

Fig 4.1 shows the FTIR spectrum of a) HKUST-1 b) CuO NPs c) CuO@HKUST-1. The spectrum of HKUST-1 shows the existence of C=O asymmetric band at wave number

1649.90  $\text{cm}^{-1}$  which corresponds to the stretching vibration of C=O, which exist at around 1709.43  $\text{cm}^{-1}$  in the ligand BTC before coordinating. This band is found at the same wave number in literature [9]. This indicated that deprotonation process occurred in C=O bond showing that the carboxylate ion participated in the complex formation. An aromatic (C=C) band was observed at 1101.28  $\text{cm}^{-1}$  and at 1372.44 a C-O band was observed which is from the BTC ligand, it may be a Cu-O stretching which is a result of the coordination of the oxygen atom with  $\text{Cu}^{2+}$ . Absorption bands at 730.81  $\text{cm}^{-1}$  may be as a result of free product of CuO. Lastly a band of C-CO<sub>2</sub> was observed at 488.92  $\text{cm}^{-1}$  [35]. These results correlated with the ones from literature; hence synthesis of HKUST-1 was a success.

The spectrum for CuO showed a band at wave number 1638.88  $\text{cm}^{-1}$  which maybe for the Cu-O symmetrical stretching. The vibration modes of CuO -NPs band are in the range the range 500-700  $\text{cm}^{-1}$  in literature [34]. From the spectrum the band is represented by the peak of wave number 527.70  $\text{cm}^{-1}$ . However since only one peak is existing in the range mentioned above, it cancels out the existence of Cu<sub>2</sub>O. From the results CuO nanoparticles were successfully synthesised.

The CuO@HKUST-1 composite had the same bands as in the HKUST-1 MOF. It only showed a shift in the wave number of these bands. This may have been attributed to the encapsulation of CuO NPs without a new band being formed [16].

## **4.2 Studies**

Studies were carried out to determine how different parameters affect the degradation of MB by HKUST-1 and CuO@HKUST-1. A solution of 20mg/L of MB was prepared and used for all the studies that were carried out. UV-VIS readings were scanned in the range 400 to 800 nm. The peak for MB was found at 663nm. Standard solutions were prepared in the range 5

to 20 mg/L for calibration of the instrument [16]. The UV-VIS calibration readings for MB are shown in table B1 calibration curve is shown in fig B1 in appendix B.

#### 4.2.1 Effect of contact time on degradation of MB by HKUST-1 and CuO@HKUST-1

The optimum time required for complete degradation of MB to take place was studied. Samples were analysed using the UV-VIS after every 30 minutes to note the change in MB absorbance with respect to time. The graph of percentage degradation of MB against time was plotted and this showed the optimum time required for maximum degradation to occur. The equilibrium data is shown in table B2 in appendix B.

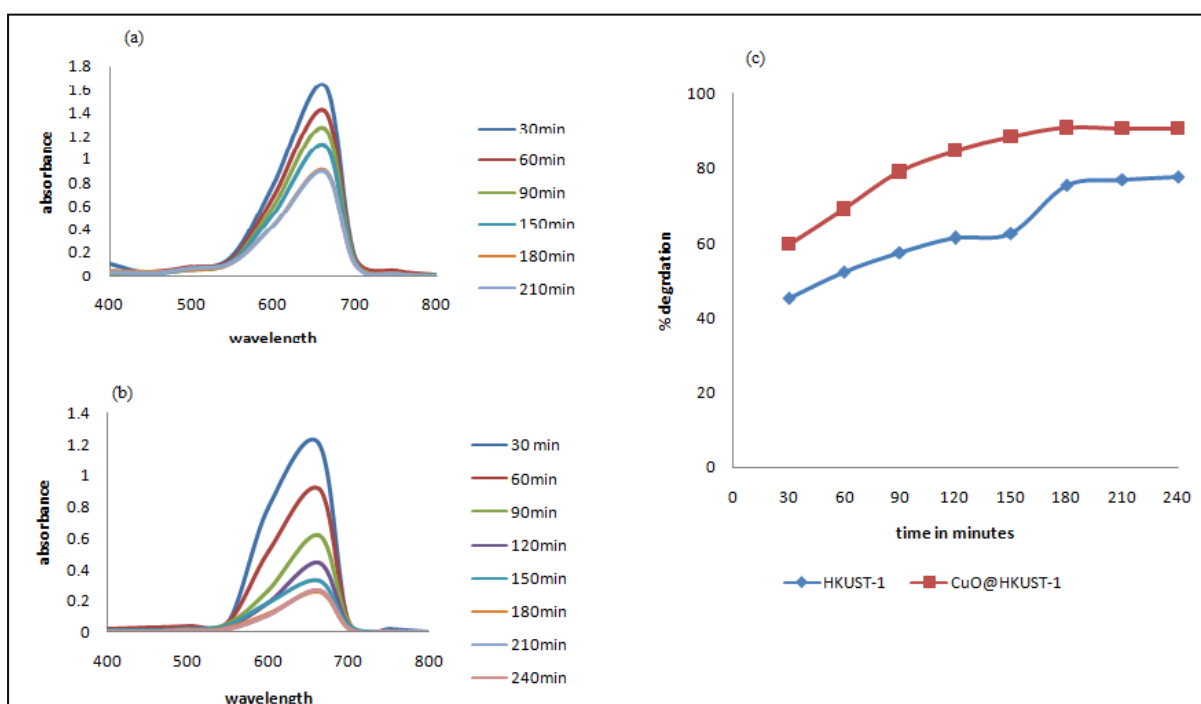


Fig 4.2 a) MB degradation using HKUST-1 between 30 – 240 minutes (b) MB degradation using CuO@HKUST-1 between 30 – 240 minutes (c) Effect of contact time on % degradation

As shown in fig 4.2 the absorbance of methylene blue was found to decrease with an increase in time for both catalysts. The percentage degradation for HKUST-1 and CuO@HKUST-1 was 45 % and 59 % respectively within the first 30 minutes upon exposure to sunlight. This

shows that initially there were a high number of active sites available for photocatalysis; absorbance was lower in CuO@HKUST-1 due its larger surface area and a higher number of catalytic sites [5]. However beyond 30 minutes all active sites had been occupied and reaction increased steadily up to the optimum time of 180 minutes. The active species, the hydroxyl ions and super oxide had to degrade the MB in contact with the catalyst and release the products first before attacking other pollutants for degradation, therefore the rate of degradation slowly decreased after the first 30 minutes [12]. Beyond 180 minutes the percentage degradation became constant showing that at that point complete degradation of MB had been achieved at 75 % and 90 % for HKUST-1 and CuO@HKUST-1 respectively.

#### **4.2.2 Effect of pH on the degradation of MB by HKUST-1 and CuO@HKUST-1**

pH is a very important parameter in photocatalytic degradation as this affects the electrostatic interactions between the catalyst and the pollutant [38]. Photocatalysis is a process that is strongly dependent on the pH of the solution. The acidity and basicity of a solution is very important for good degradation efficiency. The performance of reactive species in photocatalysis can easily be altered by the change in pH. Experiments were carried out under the same conditions only varying pH range from 2 to 10. The equilibrium data obtained is shown in table B3 in appendix B.



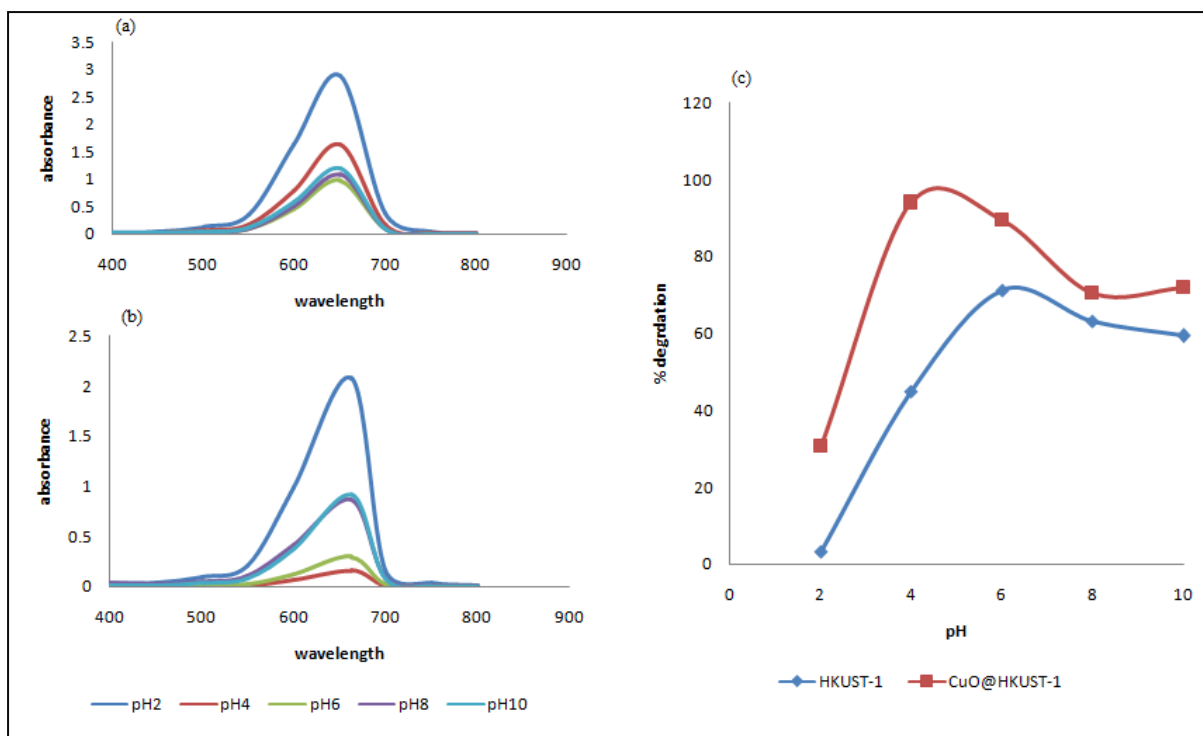


Fig 4.3 (a) MB degradation using HKUST-1 at pH 2 -10 (b) MB degradation using CuO@HKUST-1 at pH 2 -10 (c) Effect of pH on % degradation

As shown in fig 4.3, the MB absorbance was lowest at pH 6 and pH 4 for HKUST-1 and CuO@HKUST-1 respectively. At higher and lower pH values the absorbance was found to be higher. The optimum percentage degradation was found to be 71 % and 94 % for HKUST-1 and CuO@HKUST-1 respectively. For both catalysts, at very low pH of 2, the surface of the catalysts will be positively charged, as a result, there was electrostatic repulsive force between photocatalyst and cationic MB which inhibit higher binding between the two surfaces hence decreased photodegradation to as low as zero. Photocatalysis takes place in the absorbed not desorbed state, however repulsion between pollutant and catalyst will inhibit absorption hence a decrease in photocatalysis [13].

For CuO@HKUST-1, pH 4 resulted in higher percentage degradation, indicating that the stability of the solution was highest in this range; at that pH there were stronger electrostatic attraction which enhances degradation efficiency. The absorption of MB was found to be at a

maximum of pH 4, however excess  $H^+$  ions were found to decrease the rate of reaction. In alkaline conditions, complexation reaction is not favoured because of competitive adsorption by hydroxyl groups and dye molecule [16].

However, pure HKUST-1 showed a maximum degradation percentage at a pH of 6 showing that the reaction is favoured by a region close to neutral conditions where solution had a balance in  $H^+$  and  $OH^-$  ions. At the point of zero charge for a catalyst adsorption will be at its minimum [38]. The pH at point of zero charge for HKUST-1 has been reported to be 4; therefore pH 4 was not favourable for pure HKUST-1 degradation of MB.

#### **4.1.4 Effect of dosage on the degradation of MB by HKUST-1 and CuO@HKUST-1**

The effect of the photocatalyst dosage on degradation of methylene blue was investigated. An increase on the photocatalyst dosage increases the number of active sites therefore this could give a positive result. However, higher dosages might also interact with the passage of light into solution therefore the optimum amount of photocatalyst to be used for degradation of 20 mg/L MB at 180 minutes was investigated. The equilibrium data obtained was recorded in table B4 in appendix B.

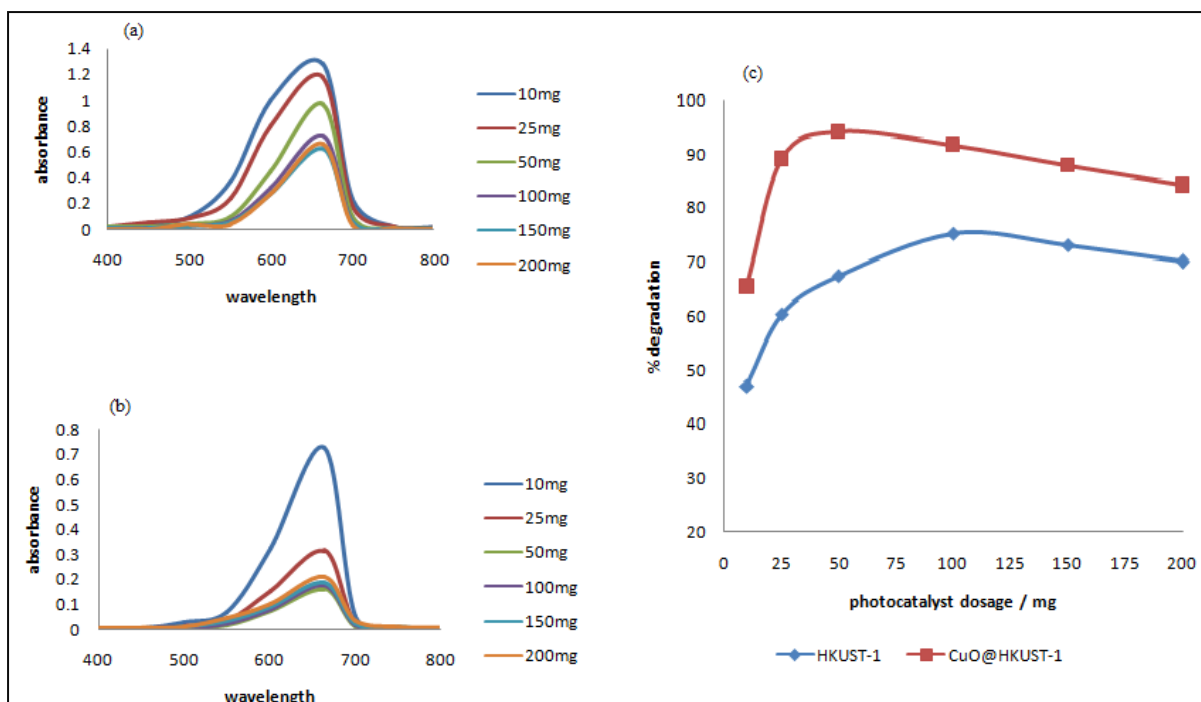


Fig 4.4 MB degradation using 10 – 200 mg HKUST-1 (b) MB degradation using 10 – 200 mg CuO@HKUST-1 (c) Effect of catalyst dosage on % degradation

The absorbance of MB was found to decrease as the amount of catalyst was increased as shown in the graphs in fig 4.4. However, beyond 50 mg and 100 mg for CuO@HKUST-1 and HKUST-1 respectively, the absorbance of MB was found to increase. Therefore percentage degradation increased with an increase in the dosage of catalyst up to a stage where the degradation is optimum, 50 mg for CuO@HKUST-1 and 100mg for HKUST-1. This is due to an increase in surface area hence production of hydroxyl radicals and super oxides increased thus an increase in degradation [27]. However as the dosage kept increasing there was a slight decrease in the degradation efficiency which could be attributed to the hindrance of proper passage of light into the solution due to the large amount of catalyst dispersed in solution. The turbidity of the solution increases and this blocks UV radiation, resulting in less a decrease in the degradation process [38].

Percentage degradation for CuO@HKUST was high, 90% at 50 mg whereas the percentage degradation was lower for HKUST-1, 75 % at a higher dosage of 100 mg. this could be due to the larger surface area to volume ratio of CuO@HKUST-1. There is also an increase in the number of active sites as a result of encapsulating CuO NP into the MOF, therefore less amount was needed to achieve complete degradation in CuO@HKUST-1 than in HKUST-1.

#### 4.1.5 Effect of initial dye concentration on the degradation of MB using CuO@HKUST-1 and HKUST-1

An increase in the initial dye concentration allows more interaction between the pollutant and the catalyst. However photocatalysis is also dependent on the passage of light through the solution, passage of light is affected by the concentration of the solution as well. Examination of the effect of initial dye concentration on the degradation of MB was carried out in the range 10-40 mg/L. The equilibrium data obtained is shown in table B5 appendix B.

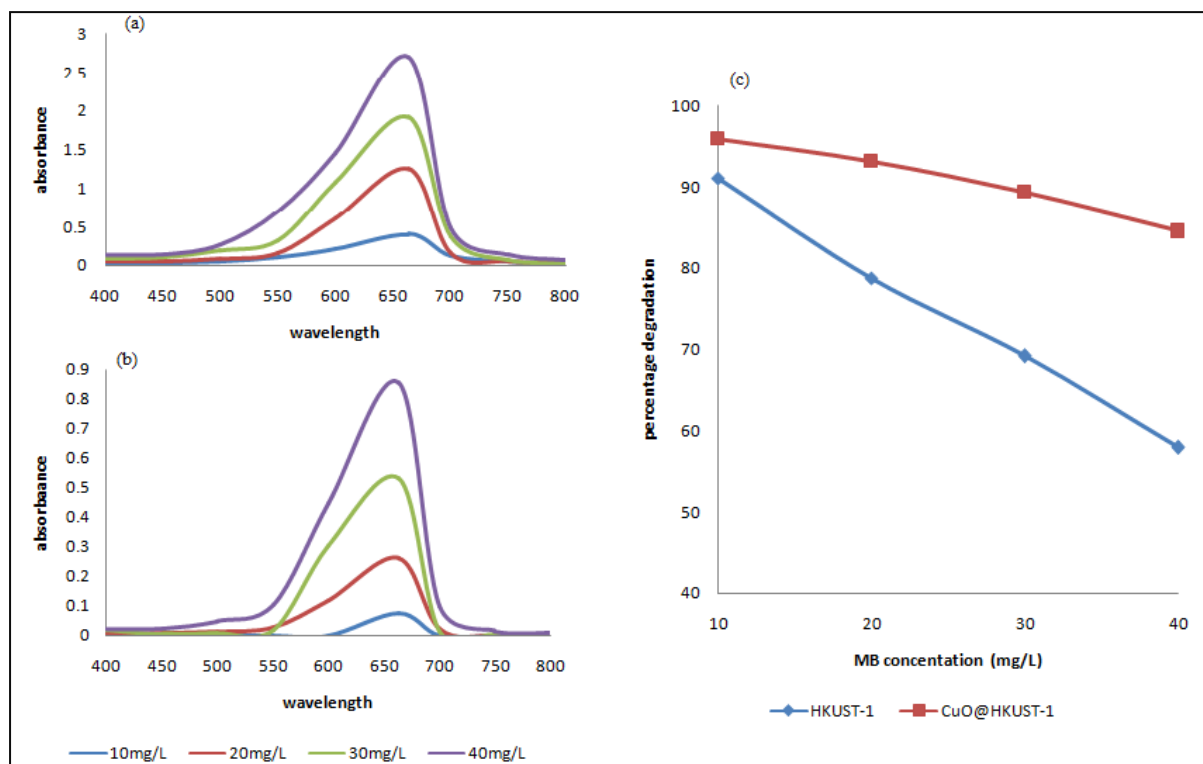


Fig 4.5 (a) MB (10 – 40 mg/L) degradation using HKUST-1 (b) MB (10 – 40mg/L) degradation using CuO@HKUST-1 (c) Effect of initial dye concentration on % degradation

The absorbance of MB at the optimum time of 180 minutes was found to increase with an increase in initial dye concentration as shown in fig 4.5. The highest percentage degradation of more than 90 % for both CuO and CuO@HKUST-1 was found at 10 m g / L. As the initial concentration of MB increased there was a decrease in the percentage degradation of MB.

These differences could be due to the light screening properties of methylene blue. An increase in the concentration of dye molecule results in an increase in the organic substances being adsorbed whereas less number of photons will be available to reach the catalyst and therefore less hydroxyl ions are formed [39]. When the concentration of methylene blue is high, the number of activated photocatalyst per molecule of dye is reduced. An increase in concentration causes it to become thicker and darker, therefore light will not pass through the solution easily hence a decrease in the photocatalytic degradation percentage [31].

#### **4.2 Degradation of MB using HKUST-1 and CuO@HKUST-1 at optimum conditions**

From the studies carried, it showed that the most efficient photocatalytic degradation of MB was at pH4, initial concentration of 20 ppm MB and 50 mg of CuO@HKUST-1. Whereas for HKUST-1 the optimum conditions were found at pH 6, initial dye concentration of 20 ppm and 100 mg of catalyst, the degradation process was the carried out at the optimised conditions respectively. Data obtained and calculated was recorded in table B6 in appendix.

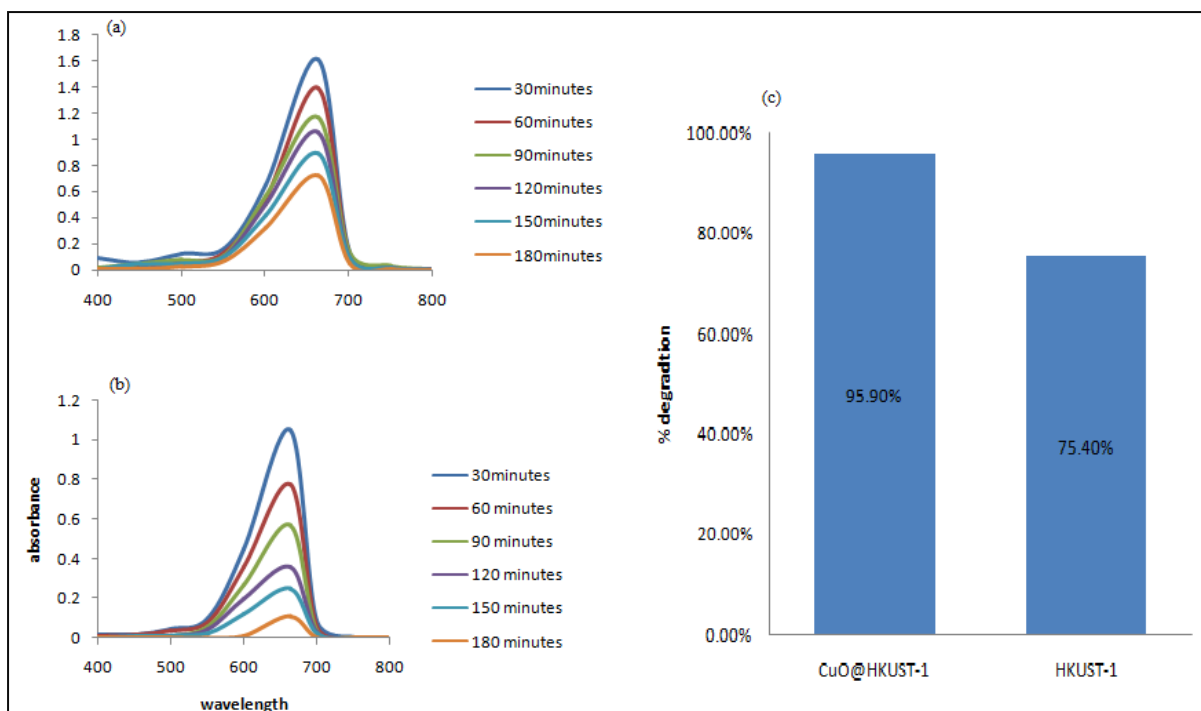


Fig 4.6 (a) MB degradation using HKUST-1 at optimum conditions (b) MB degradation using CuO@HKUST-1 at optimum conditions (c) Degradation efficiency of HKUST-1 and CuO@HKUST-1 at optimum conditions

The results for MB degradation are shown in fig 4.6. CuO@HKUST-1 showed better photocatalytic properties and resulted in 95.9 % MB degradation whereas HKUST-1 resulted in 75.4 % MB degradation. The better performance of CuO@HKUST-1 could be as a result of increase in surface area of the catalyst, reduced band gap energy hence absorption of light in the visible range, reduction in the electron-hole recombination and an increase in the number of active sites [40].

### 4.3 Kinetic studies

The most commonly used kinetic model for heterogeneous photocatalysis, pseudo first order model was used to test the degradation kinetics of MB by HKUST-1 and CuO@HKUST-1. It was used to determine the rate controlling mechanism of the degradation process. This was done by monitoring the rate at which MB was degraded and removed from solution from 30

minutes to 180 minutes. The fitting of the kinetic model to the experimental data was evaluated using the magnitude of the correlation of determination ( $R^2$ ) [41].  $R^2$  values which were greater than 0.9 were accepted as portraying fitness to the model. Calculated data is shown in table B7 in appendix B.

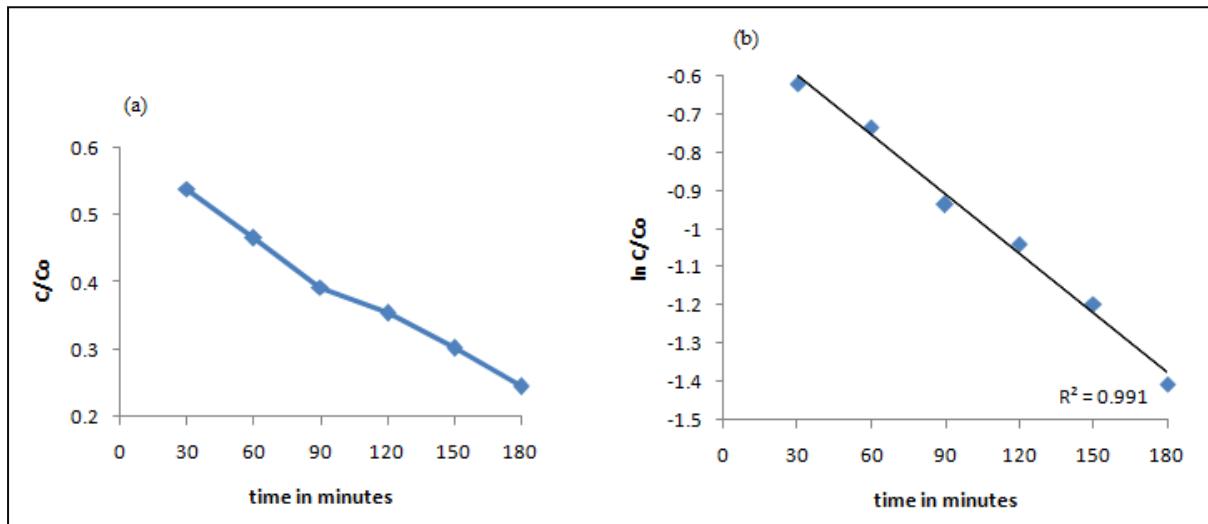


Fig 4.7 (a) Change in MB concentration against time using HKUST-1 (b) Pseudo 1<sup>st</sup> order model for degradation of MB by HKUST - 1

Fig 4.7 shows the pseudo 1<sup>st</sup> order kinetics plot of  $\ln (C/Co)$  against time from which the rate constant and activation energy was calculated. The rate constant  $K/\text{min}$  was found to be 0.008 and the activation energy was found to be 12.125 k j/mol.

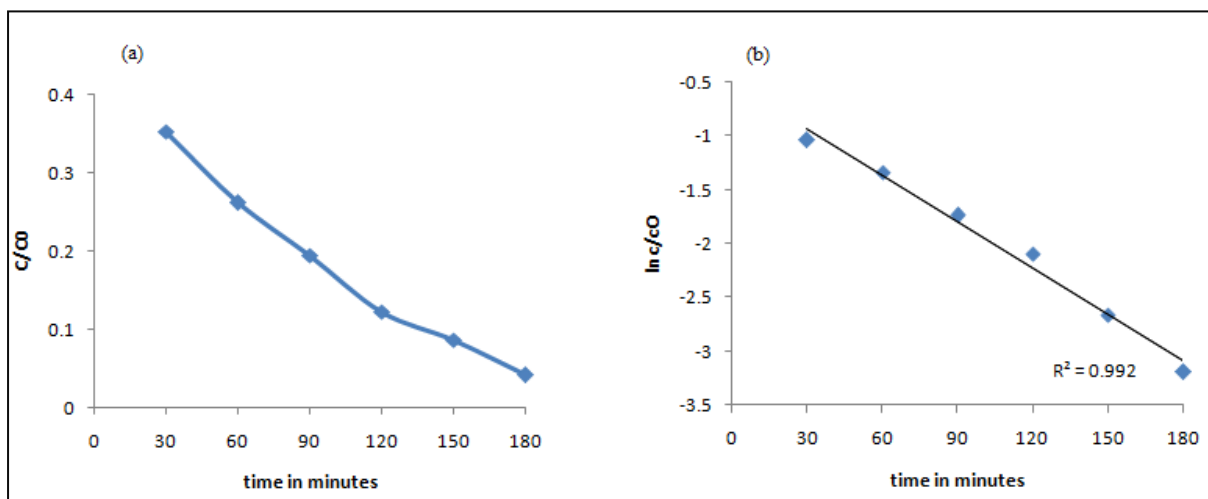


Fig 4.8 (a) Change in MB concentration against time using CuO@HKUST-1 (b) Pseudo 1<sup>st</sup> order kinetics for degradation of CuO@HKUST-1

Fig 4.8 shows the pseudo 1<sup>st</sup> order kinetics plot of  $\ln(C/C_0)$  against time from which the rate constant and activation energy was calculated. The rate constant K/min was found to be 0.022 and the activation energy was found to be 9.614 k j/mol

The rate of a reaction decreases with irradiation time as it follows the pseudo first order kinetics and also there will be a competition for degradation between the reactants and intermediate products. Initially the rate degradation is very high then there is slow rate of dye degradation after a certain time as shown by the graphs of  $C_0/C$  against time. This is due to difficulty in the reaction of short chain aliphatics with hydroxyl radicals and short lifetime of catalysts as a result of active site deactivation by strong by products deposition [38].

The rate constant values show that the CuO@HKUST-1 catalysed reaction was faster than that of HKUST-1. The activation energy, the amount of energy required for a chemical reaction, was lower for CuO@HKUST- than for HKUST-1. Both reactions followed pseudo 1<sup>st</sup> order kinetic model.

#### **4.4 Effect of MB adsorption, self catalysis and photocatalytic properties using CuO@HKUST-1**

The behaviour of methylene blue under the optimized conditions in light and in darkness was evaluated; this was done to compare the adsorptive versus the photocatalytic properties of CuO@HKUST-1. MB was also checked for self catalysis properties by exposing it to sunlight for 180 minutes without adding any catalyst [37].



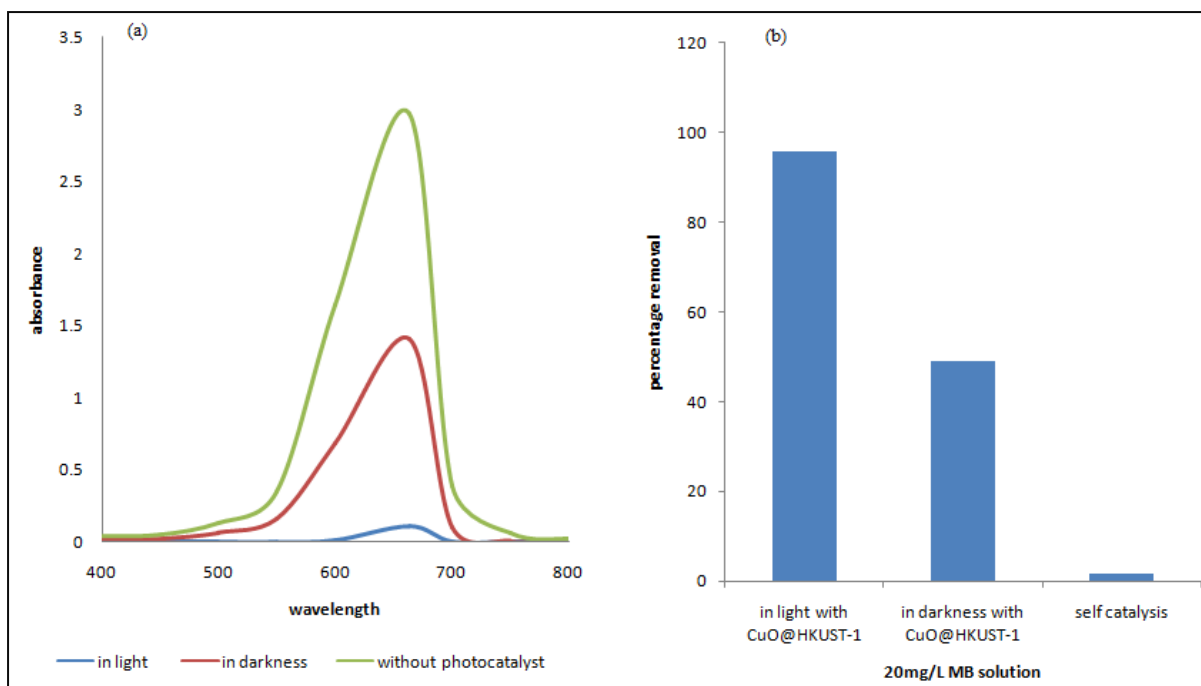


Fig 4.9 (a) MB degradation in light, darkness and without photocatalyst (b) % removal of MB during photocatalysis, adsorption and self catalysis

The results as displayed in fig 4.9 show that methylene blue is not capable of being self catalysis or self degradation under sunlight. There was a negligible change in absorbance of methylene blue after 180 minutes, showing that methylene blue dye, as reported by other researchers, is very stable to light [21].

CuO@HKUST-1 showed better degradation efficiency in sunlight than in darkness. This showed that CuO@HKUST-1 works well as a photocatalyst than as an adsorbent. CuO@HKUST-1 is capable of absorbing the solution onto its surface to facilitate the photocatalytic process. The catalyst showed good photocatalytic properties for degradation of MB.

#### 4.4 Examination of CuO@HKUST-1 reusability

A good catalyst must be stable and should remain unchanged after a reaction; therefore it should be able to produce good results after being re-used for a couple of times.

CuO@HKUST-1 was examined for its stability after being used for 4 times.

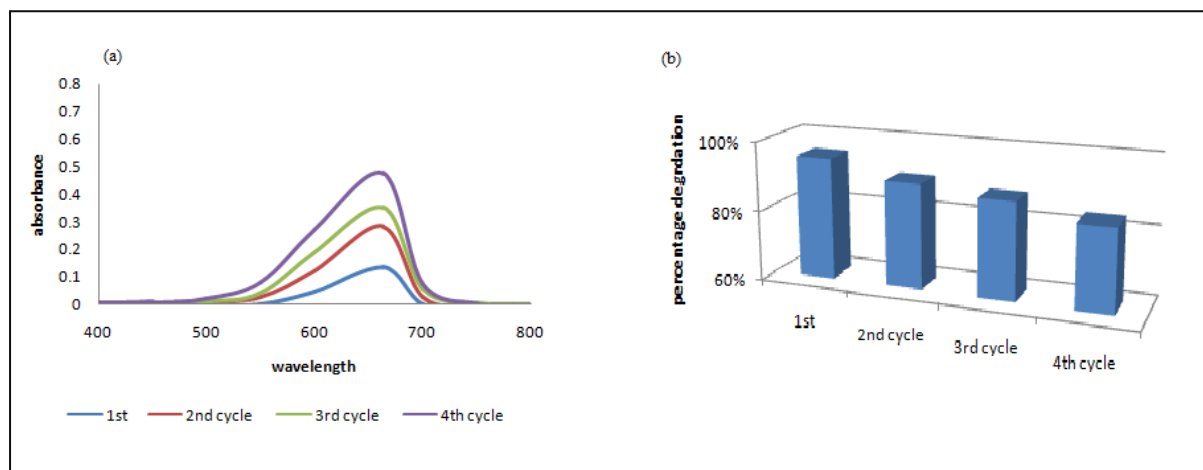


Fig 4.10 (a) MB degradation re using CuO@HKUST-1 for 4 times (b) Effect of re using CuO@HKUST-1 on MB % degradation

As shown in fig 4.10 the catalyst has good recyclability properties as it still produced a degradation efficiency of more than 80 % at its 4<sup>th</sup> cycle. This shows that CuO@HKUST-1 absorbed the MB solution onto its surface and the degradation process took place after which the catalysed released the non toxic compound, water and carbon dioxide back into the solution. Therefore the catalyst surface remained available for further degradation process. However the little decrease noted could be due to clogging of the catalyst surface by some ions from the solution [16]. Inorganic ions present in waste water such as calcium, chlorides, nitrates and sulphides affect photocatalytic degradation rate as they can be adsorbed onto the surface of the catalyst thus competing with methylene blue hence a decrease in the active sites. It reduces the stability, increases mass transfer, and reduces surface contact between pollutant and the photocatalyst [12].

#### 4.4.1 Characterisation of re-used catalyst

The CuO@HKUST-1 catalyst was analysed by FTIR after each cycle. This was done to see the changes in the vibrations up to the 4<sup>th</sup> time of being reused. Any changes in the major functional groups of CuO@HKUST-1 were analysed to check for stability of the catalyst.

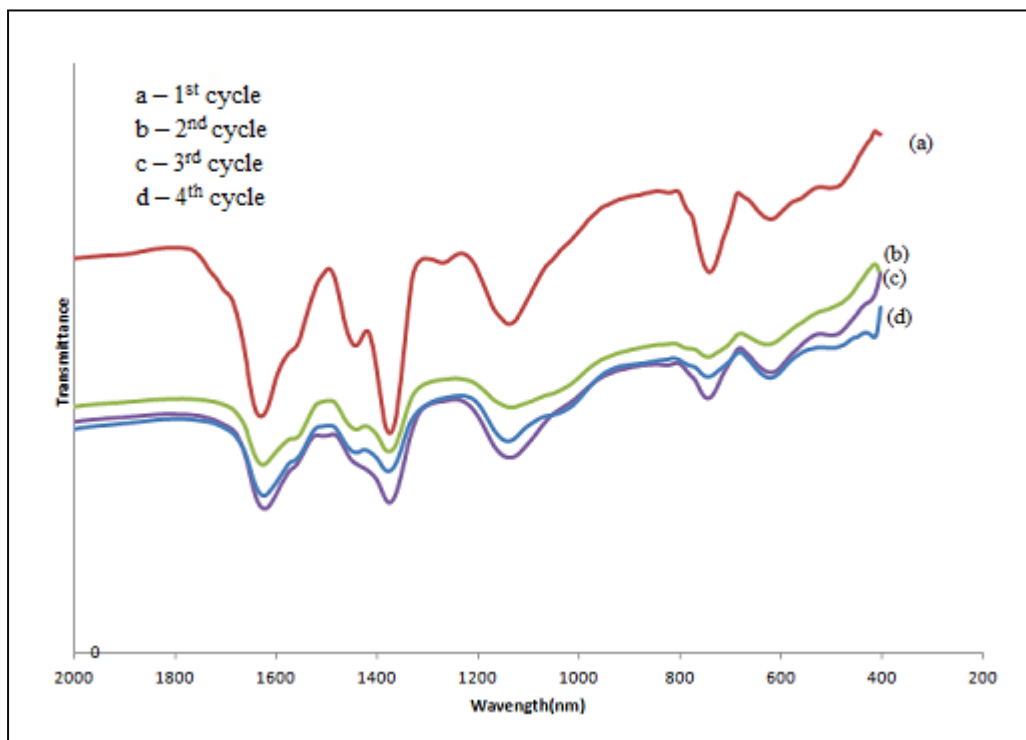


Fig 4.11 FTIR spectra for re used CuO@HKUST-1

Fig 4.11 shows that the functional groups were retained however, the intensity of the peaks was found to decrease gradually from first to fourth cycle. The CuO nanoparticles remained in the porous HKUST-1 throughout the process as evidenced by the presence of Cu-O band (found in the range 500 – 700) throughout the cycles. The changes in the intensity of the peaks could be due to the clogging of the surface of the catalyst by nitrates, chlorides, carbonates and sulphates [38]. These ions scavenge the holes and hydroxyl ions. The decrease in peak intensity could also be due to the adsorption of some MB molecules onto the surface of the catalyst since it possesses some adsorptive properties.

## CHAPTER 5

### CONCLUSION AND RECOMMENDATIONS

#### 5.1 Conclusion

The current study focused on the synthesis of HKUST-1 and the encapsulation of CuO NP into HKUST-1 MOF. The synthesis was successfully carried out and catalysts were applied towards degradation of MB. Optimum conditions for degradation of 20 ppm MB by HKUST-1 were found to be catalyst dosage of 100 mg, pH 6 and contact time of 180 minutes. Optimum conditions for degradation of 20 ppm MB by CuO@HKUST-1 were found to be catalyst dosage of 50 mg, pH 4 and contact time of 180 minutes. The percentage degradation was found to decrease as the concentration of initial dye concentration increased. The pseudo first order model suited the degradation of methylene blue by both HKUST-1 and CuO@HKUST-1 with an  $R^2$  value of 0.991 and 0.992 respectively. On the recovery and reuse of CuO@HKUST-1, the results showed that CuO@HKUST-1 can be reused for 4 cycles producing results which are above 80%. Therefore CuO@HKUST-1 is a stable photocatalyst, characterisation after reuse showed that the composite maintained its main functional groups and only showed a decrease in the intensity of the peaks.

#### 5.2 Recommendations

- HKUST-1 and CuO@HKUST-1 should be applied towards degradation of other types of pollutants
- The degraded products of MB must be analysed for identification
- Possible interruptions in the degradation of methylene blue by HKUST-1 and CuO@HKUST-1 should be investigated

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## APPENDIX

### APPENDIX A

TABLE A1 REAGENTS

<b>Chemical name</b>	<b>Chemical formula</b>	<b>Mass/Concentration</b>
Benzene-1,3,5-tricarboxylic acid	H <sub>3</sub> BTC	0.45g
Copper chloride	CuCl <sub>2</sub>	5.6g
Dimethylformamide	DMF	200 m L
Sodium hydroxide	NaOH	9.6g and 0.02M
Hydrochloric Acid	HCl	0.02
Distilled water	H <sub>2</sub> O	-
Ethanol	C <sub>2</sub> H <sub>5</sub> OH	75%
Methylene blue	C <sub>16</sub> H <sub>18</sub> ClN <sub>3</sub> S	-
Sodium chloride	NaCl	0.02M

TABLE A2: INSTRUMENTATION

<b>Instrument</b>	<b>Model</b>	<b>Manufacturer</b>	<b>Use in experiment</b>
Analytical balance	PWL 84	AE Adam	Weighing samples
Hot plate and stirrer	MSH10	LABCON	Heating and stirring
Centrifuge	Labofuge 200	Sepatech	Separating samples
Oven	DHG GO70A	Zenith	Drying amples
Muffle furnace	L-1200	LABEX	Calcinating samples
UV-Visible	756	-	Measuring the adsorbance
Fourier Transform Infra-red Spectrophotometer	Nicolet 6700	ThermoScientific	Bond vibrational frequency determination

APPENDIX B

TABLE B1 Calibration results for UV-VIS spectrophotometer

Concentration of MB (mg/L)	Absorbance
0	0
5	0.688
10	1.549
15	2.345
20	3.000

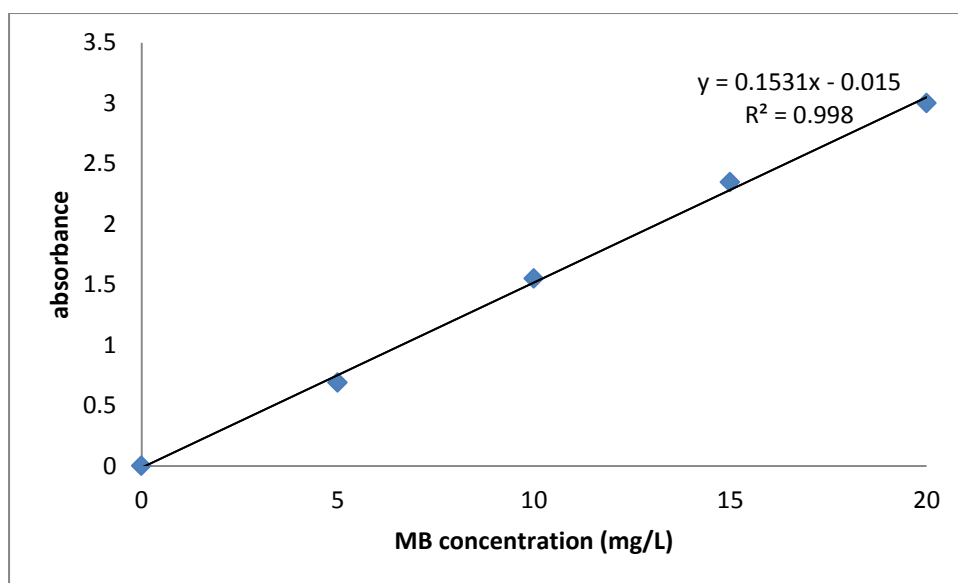


Fig B1 calibration curve for degradation of MB by HKUST-1 and CuO@HKUST-1

TABLE B2 Equilibrium data for the effect of contact time on MB degradation

time	absorbance at 663 nm		concentration		% degradation	
	HKUST-1	CuO@HKUST-1	HKUST-1	CuO@HKUST-1	HKUST-1	CuO@HKUST-1
30min	1.638	1.202	10.80	7.95	45.2	59.6

60min	1.420	0.916	9.38	6.08	52.4	69.1
90min	1.268	0.621	8.39	4.16	57.4	79.0
120min	1.153	0.445	7.63	3.01	61.3	84.7
150min	1.114	0.332	7.38	2.27	62.6	88.5
180min	0.902	0.262	5.99	1.81	75.4	90.8
210min	0.895	0.268	5.95	1.85	76.9	90.6
240min	0.898	0.271	5.97	1.87	77.6	90.5

TABLE B3: Equilibrium data for effect of pH on degradation of MB

pH	absorbance at 663 nm		concentration		% degradation	
	HKUST-1	CuO@HKUST-1	HKUST-1	CuO@HKUST-1	HKUST-1	CuO@HKUST-1
2	2.899	2.078	19.05	13.74	3.3	30.6
4	1.638	0.162	10.80	1.16	45.0	94.1
6	0.848	0.298	5.64	2.05	71.3	89.6
8	1.093	0.870	7.24	5.78	63.3	70.6
10	1.209	0.833	8.0	5.54	59.4	71.9

TABLE B4: Equilibrium data for effect of catalyst dosage on degradation of MB

dosage	absorbance at 663 nm		concentration		% degradation	
	HKUST-1	CuO@HKUST-1	HKUST-1	CuO@HKUST-1	HKUST-1	CuO@HKUST-1
10mg	1.282	0.726	8.48	4.84	57.0	75.4
25mg	1.179	0.315	7.80	2.15	60.4	89.1

50mg	0.969	0.162	6.43	1.66	67.4	94.1
100mg	0.726	0.175	4.84	1.24	75.4	93.7
150mg	0.621	0.190	4.16	1.34	79.0	93.2
200mg	0.659	0.210	4.41	1.47	77.6	92.5

TABLE B5: Equilibrium data for the effect of initial [MB] on degradation of MB

initial	absorbance at 663 nm		concentration		% degradation	
	HKUST-1	CuO@HKUST-1	HKUST-1	CuO@HKUST-1	HKUST-1	CuO@HKUST-1
10mg/L	0.404	0.077	3.67	1.70	91.1	95.9
20mg/L	1.251	0.262	8.78	2.82	78.8	93.2
30mg/L	1.923	0.534	12.82	4.46	69.2	89.3
40mg/L	2.705	0.855	17.54	6.39	57.9	84.6

TABLE B6: Equilibrium data for the degradation of MB at optimum conditions

photocatalyst	Absorbance of MB	Concentration of MB	% degradation of MB
CuO@HKUST-1	0.11	0.81	95.9
HKUST-1	0.726	4.82	75.4

TABLE B7: Equilibrium data for kinetic studies for degradation of MB

catalyst	Time/minutes	% degradation	Rate K/min	Ea(KJ/mol)
CuO@HKUST-1	180	95	0.022	9.611
HKUST-1	180	75	0.008	12.166

TABLE B8: Equilibrium data for photocatalytic degradation, adsorption and self catalysis of MB

	Absorbance	Concentration	% degradation
In light	0.11	0.81	95.9
In darkness	1.405	9.23	53.1
Self catalysis	2.971	19.4	1.5

TABLE 9: Equilibrium data for reusability of CuO@HKUST-1 for MB degradation

	Absorbance	Concentration	% degradation
1 <sup>st</sup>	0.135	0.975	95.0
2 <sup>nd</sup> cycle	0.282	1.9306	90.2
3 <sup>rd</sup> cycle	0.406	2.7383	86.1
4 <sup>th</sup> cycle	0.7	4.6509	76.4