

University of Zimbabwe Faculty of Science, Chemistry Department

Purification of water using surface engineered zeolites

A dissertation submitted in partial fulfilment of the requirements for the Master of Science in Chemistry

By

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I declare that this dissertation entitled "Purification of water using surface engineered zeolites" is an original document and a product of my efforts. Where use of other people's work has been made, it has been duly acknowledged. This work has not been submitted in part or in whole to any university in any degree.

Signature

Approved by

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This work is dedicated to my mom Ever K Munetsi and my dad Edmore Matseketsa.

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ABSTRACT

Coal fly ash obtained from Coca Cola Company in Harare was utilised in synthesis of zeolites by hydrothermal method using 3M NaOH. The Ze-ZnO nanoflakes and Ze-ZnO nanorods were successfully synthesised using a combination of hydrothermal and one pot homogeneous precipitation method. The zeolitic materials were characterised by FT-IR, BET SEM, XRD and EDX. The Ze-ZnO nanoflake and Ze-ZnO nanorod samples were tested for heavy metal removal capacity by using 300 ppm of Cd and Pb. The adsorption experiment was done using 0.2 g of the Ze-ZnO nanoflakes and Ze-ZnO nanorods under mechanical shaking for 60 mins. The Ze-ZnO nanoflakes proved to be efficient in the removal of heavy metals with adsorption capacities of 74 mg/g and 15.5 mg/g for Pb and Cd respectively compared to 62.5 mg/g and 11.3 mg/g with Ze-ZnO nanorods. The photocatalytic activities of Ze-ZnO nanorods and Ze-ZnO nanoflakes were tested using methylene blue dye as model pollutant under UV irradiation. The degradation efficiencies of Ze-ZnO nanorods and Ze-ZnO nanoflakes were almost the same, 95.61% and 96.87% respectively. The adsorption of heavy metals and degradation of MB dye on Ze-ZnO nanorods followed pseudo second order kinetics. The photocatalytic activities of Ze-ZnO nanoflakes and Ze-ZnO nanorods fitted in the first order kinetic plot. The adsorption isotherms of Pb, Cd and methylene blue dye fitted perfectly into the Langmuir isotherm. The multifunctional characteristics of Ze-ZnO nanorods were established and these included adsorption and photo degradation therefore it can qualify as an alternative to existing water treatment methodologies.

LIST OF ABBREVIATIONS

EDS	: Energy	dispersive	X-ray	spectrosco	ру
	0,	1	2	1	

- FT-IR : Fourier –transform infrared spectroscopy
- MB dye : Methylene blue dye
- SEM : Scanning electron microscopy
- UV-Vis : Ultraviolet visible spectroscopy
- XRD : X-Ray Diffraction
- Ze-ZnO NF : Zeolites modified with ZnO nanoflakes
- Ze-ZnO NR : Zeolites modified with ZnO nanorods

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1.1 Background Information

The most valuable resource in the world is water. The world however, is facing a water crisis. Rapid industrialisation, uncontrolled population growth and civilisation are some of the major reasons which led to increased water pollution to such a degree that it can no longer be considered safe for use without prior treatment (Shikha et al., 2017). The main significant materials which have been developed to address this problem include membranes, porous materials and zeolites but they have a drawback of addressing a specific category of contaminants and lack multifunctional characteristics. Reverse osmosis membrane filtration is one of the most common techniques currently used in simultaneous removal of major water contaminants (Lauren et al., 2008, Ruchi et al., 2016. However, it suffers from bio-fouling while generating a significant quantity of reject water. In addition, the technique is costly and requires a lot of energy. Metal nanoxides have also been employed for simultaneous removal of heavy metals and organic pollutants thus possessing multifunctional character (Ibrahim et al., 2017). They however remove heavy metals at low efficiency. According to Alvarez-Ayuso, 2003, several studies of zeolites have confirmed their excellent performance on the removal of metal cations from wastewaters. On the other hand, photocatalytic metal oxides have been widely used in the photo-degradation of various toxic organic pollutants in water as well as for their antibacterial characteristics. However, they still cannot purify different classes of contaminants at high efficiency and this makes water purification costly and paves way for the development of alternatives which can simultaneously remove all classes of contaminants at a more economical level. In an attempt to do this, Ruchi et al., 2016), developed surface engineered zeolites by incorporating zinc oxide nano-particles in the form of ZnO nano-flakes to form novel materials capable of simultaneously removing Pb(II), methylene blue, E.coli, Aureus and Pseudomonas from contaminated water. The material is multifunctional, efficient, nontoxic, energy neutral and recyclable with no effluent generation thus making it a sustainable alternative for water purification. However, the material can be further improved by incorporating ZnO nanorods which have a large surface area compared to the ZnO nanoflakes due to porous nanoholes on their surface (Ismail et al., 2015). The adsorption properties of nanorods are therefore expected to be better due to the presence of nanoholes which increase their surface area compared nano-flakes which will have relatively small surface area.

Therefore, the aim of this project is to modify zeolites with ZnO nanorods so as to optimise the properties for adsorption of water contaminants.

1.2 Problem Statement

Current water treatment methods can only remove one type of contaminant at a time which makes the water purification process costly. Metal nanoxides have been employed for simultaneous removal of heavy metals and organic pollutants thus possessing multifunctional character (Ibrahim et al., 2017). However, the sorption capacity of ZnO nanoparticles is very low (26.11mg/g for Pb), (Dubey et al., 2017) compared to synthetic zeolites (45.96mg/g for Pb) (Ruchi et al., 2016). This means that even though ZnO nanoparticle can be used for simultaneous removal of heavy metals and organic pollutants, there is need for improvement for efficient water purification.

According to Alvarez-Ayuso, 2003, several studies of zeolites have confirmed their excellent performance on the removal of metal cations from wastewaters. On the other hand, photocatalytic metal oxides have been widely used in the photo-degradation of various toxic organic pollutants in water as well as for their antibacterial characteristics. Studies have proven that modifying zeolites with ZnO nanoflakes enabled the simultaneous removal of heavy metals and organic waste (Ruch et al., 2016). The material is multifunctional, efficient, nontoxic, energy neutral and recyclable with no effluent generation thus making it a sustainable alternative for water purification.

No studies have been reported for modification of zeolites with ZnO nanorods. Ismail and coworkers, 2015, showed that ZnO nanorods have porous nanoholes on their surface. The adsorption properties of nanorods are therefore expected to be better due to the presence of nanoholes which increase their surface area compared nano-flakes which will have relatively small surface area. As a consequence, there is need to test if modifying zeolites with ZnO nanorods will result in a material that is highly efficient compared to the zeolites modified with ZnO nanoflakes. This project aims to develop a novel material which is capable of removing contaminants simultaneously.

1.3 Knowledge Gap

A recent research by Ruchi and co-workers, 2016 showed that modifying zeolites with ZnO nano-flakes resulted in a material which is capable of simultaneous removal of both organic pollutants and heavy metals. Ismail and others, 2015 found out that ZnO nanorods have porous holes on their surface which were believed to increase the surface area. No studies have been reported where zeolites have been modified with ZnO nanorods for water purification. Therefore, a novel material with multifunctional characteristics for water purification is going to be synthesised by incorporating ZnO nanorods onto the zeolite surface.

1.4 Justification

Wastewater purification and treatment has always been a challenge to mankind due increased population and industrialisation. The wastewater from industries contains chemicals which are harmful to aquatic life and humans and these include dyes and heavy metals. These chemicals are highly toxic and non-biodegradable, hence their removal from wastewater is a major task and this has led to shortage of clean water supply to communities because of high cost of chemicals for water purification. Many researchers have developed several materials including membranes, porous materials, zeolites and nano oxides in trying to address this problem. In this research, ZnO nanorods were incorporated into the zeolite structure to obtain a multifunctional material where the zeolite core contributes to the high adsorption of heavy metals, while the ZnO nanorods facilitate photodecomposition of organic matter, provides antibacterial characteristics and impart negative surface charge to enhance adsorption. It provides additional benefits of easy separation and easy recyclability. This will benefit the community at large as there will be a decrease in deadly diseases like cancer which is potentially caused by heavy metals.

In addition to the cost problem, another important factor pushing towards low-cost adsorbents is the use of disposed coal fly ash in order to reduce the cost of disposal and minimise the environmental impact of waste materials without introducing into the environment new materials. This research utilised waste coal fly ash which is regarded as a nuisance in the environment. The utilisation of the coal fly ash to make modified zeolites will help the society to grade their waste, thereby increasing waste management strategies.

1.5 Aims and Objectives

1.5.1 Aim

• The aim of this project is to modify zeolites with ZnO nanorods in order to produce a novel material with multifunctional properties in the removal of water contaminants.

1.5.2 Objectives

- 1. To synthesise zeolites from coal ash fly.
- 2. To modify the synthesised zeolites with ZnO nanorods.
- 3. To modify the synthesised zeolites with ZnO nanoflakes
- 4. To characterise the zeolites and ZnO nanorods modified zeolites.
- 5. To evaluate the efficiency of the prepared Ze-ZnO photo-catalyst adsorbent in the removal of heavy metals (Pb²⁺, Cd²⁺) and organic dye (methylene blue) from water.

1.6 Research Questions

- 1. Will the Ze-ZnO nanorods possess multifunctional properties?
- 2. Are Ze-ZnO nanorods more efficient compared to the Ze-ZnO nanoflakes?
- 3. Can the Ze-ZnO nanorods be used as an alternative method for water purification?

1.7 Literature Review

Wastewater treatment and purification has always been a problem and is actually becoming worse due to increased population and industrialisation (Shikha et al., 2017). A lot of work has been done on the development of innumerable materials for water treatment. The most common ones include membranes, porous material and zeolites. However, they suffer from lack of multifunctional character i.e. they only address a specific category of contaminants. Reverse osmosis membrane filtration is the current common technique which is capable of removing major water contaminants. Its major disadvantages are bio-fouling, expensiveness and high energy requirement. Metal nanoxides have also been employed in simultaneous removal of heavy metals and organic pollutants thus possessing multifunctional character (Ibrahim et al.,

2017). However, the sorption capacity of ZnO nanoparticles is very low (26.11 mg/g for Pb), (Dubey et al., 2017) compared to synthetic zeolites (45.96 mg/g for Pb) (Ruchi et al., 2016).

Zeolites have been considered the most important technique for heavy metal removal in water purification because of their ion exchange and sorption properties. Their structure is comprised of a framework of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra connected to each other at the corners as shown on Fig. 1(a) (Querol, 2002). Zeolites belong to a group of cation exchangers because of the negative charge on their surface, which result from the replacement of silicon by aluminium in the primary structural unit. They are selective on several toxic heavy metals, which are often present in waste waters e.g. Cu^{2+} , Ag^{2+} , Cd^{2+} , Zn^{2+} , Mo^{2+} , Cr^{3+} , Pb^{2+} , Mn^{2+} and Ni^{2+} . They are also highly selective on NH_4^+ and ion exchanges it preferably towards other competing cations. These ions are removed from water by replacing them with biologically acceptable cations such as Na^+ , Mg^{2+} , K^+ , H^+ or Ca^{2+} from the zeolite exchange sites (Margeta, 2013). The ion exchange process is a stoichiometric reaction in which one ion in the solid phase is replaced by an equivalent ion from the solution. It can be represented by equation 1 (Alshameri et al., 2014):

Where Z_A and Z_B are the charges of cations A and B respectively and symbols *z* and *s* represent zeolite and solution phases respectively.



Figure 1: (a) Idealised structure of zeolite framework of tetrahedral $[SiO_4]^{4-}$ with a Si/Al substitution ($[AlO_4]^{5-}$) yielding a negative charge, and consequently a cation exchange capacity (Querol, 2002), (b) chemical structure (Georgeiv et al, 2009)

Several types of zeolites have been synthesised and tested for heavy metal removal, such as clinoptilolite and zeolites X,Y, A and P (Li et al., 2017). A lot zeolization processes have been developed. These include, hydrothermal method, microwave assisted ageing, ultrasound assisted synthesis and sonochemical conversion (Aldahri et al., 2016). These methods are based on the dissolution of Al-Si bearing fly ash phases with alkaline solutions (consisting mainly NaOH and KOH) and the subsequent precipitation of zeolitic material (Querol et al., 2002). The formation of a specific zeolite depends on the proportions of SiO₂/ Al₂O₃ in the starting material (Izidoro et al., 2012) and the zeolization process used (Aldahri et al., 2016). Table 1 shows the proportions and the types of zeolites produced from fly ash.

Table 1: Zeolites and other neomorphic phases synthesised from coal fly ash and Joint Committee of Power Diffraction Standard (JCPDS) codes for XRD identification (Querol et al., 2002)

Zeolitic product	Formula	JCPDS
NaP1 zeolite	Na ₆ Al ₆ Si ₁₀ O ₃₂ .12H ₂ O	39-0219
Phillipsite	$K_2Al_2Si_3O_{10}.H_2O$	30-0902
K-chabazite	$K_2Al_2SiO_6.H_2O$	12-0194
zeolite F linde	KAlSiO ₄ 1.5H ₂ O	25-0619
Herschelite	$Na_{1.08}Al_2Si_{1.68}O_{7.44}1.8H_2O$	31-1271
Faujasite	Na2Al2Si3.3O8.8.6.7H2O	12-0228
zeolite A	NaAlSi _{1.1} O _{4.2} .2.25H ₂ O	43-0142
zeolite X	NaAlSi _{1.23} O _{4.46} .3.07H ₂ O	39-0218
zeolite Y	NaAlSi _{2.43} O _{6.86} .4.46H ₂ O	38-0239
Perlialite	K9NaCaAl12Si24O72.15H2O	38-0395
Analcime	NaAlSi ₂ O ₆ .H ₂ O	19-1180
hydroxy-sodalite	$Na_{1.08}Al_2Si_{1.68}O_{7.44}.1.8H_2O$	31-1271
hydroxy-cancrinite	$Na_{14}Al_{12}Si_{13}O_{51}.6H_2O$	28-1036
Kalsilite	KAlSiO ₄	33-0988
Tobermorite	$Ca_{5}(OH)_{2}Si_{6}O_{16}.4H_{2}O$	19-1364

The potential industrial application of zeolitic material is dependent upon its structure. For example, zeolite X has large pore size (7.3 Å) and a high cation exchange capacity (CEC) (5 meqg⁻¹), making it an interesting molecular sieve and a high cation exchange material (Querol

et al., 2002). Due to this high CEC, these zeolites find application in water decontamination, especially the removal of heavy metals and ammonium from solutions (Catalfam et al., 1993; Querol et al., 1997; Suyama et al., 1996; Patane et al., 1996; Lin et al., 1995; Moreno et al., 2001). However, the small pore size of hydroxyl-soldalite (2.3 Å) accounts for low potential application for both molecular sieving and ion exchange.

A lot of factors determine the actual or operating cation exchange capacity including zeolite's framework structure, the zeolite's framework electrostatic field strength, the nature of the cation and its charge density, the composition of the contacting solution, the pH of the contacting solution, the composition and work-up of the raw mineral used as a zeolite and the process apparatus and the operating conditions (Alvarez Ayuso, 2003).

Coal fly ash can be utilised in the synthesis of zeolites because most power plants whole world wide produce coal fly ash (CFA) during electricity generation, hence it is available in abundance. It was reported in literature that even though CFA is mainly used in concrete production as pozzolan, more than 50% of world's CFA is disposed of into landfills at a significant cost to the producers of this waste product (Aldahri et al., 2016). This means CFA is readily available as waste and if not used there will be accumulation of CFA leading to environmental or economic burden because CFA disposal requires large vacant land or construction of expensive ash dams (Tunde, 2016). In an attempt to solve this problem, several approaches have been studied and tested for proper utilisation of CFA to reduce cost of disposal and minimising environmental impact. One such approach is conversion of CFA to zeolites which have wider application in ion exchange, molecular sieves, catalyst and adsorbent manufacture (Chigondo et al., 2013). As a result of their surface properties, zeolites have been widely used in water purification, specifically in heavy metals removal.

The proposed mechanism for zeolites synthesis is shown in Fig. 2 (Murayama et al., 2002). The researches indicated that dissolution is the first step and occurs at the temperature rising stage between 293 K and 393 K. This results in surface particles changing from sphere to something uneven like in structure. The dissolution rate is greatly dependent on concentration of OH^- in the alkali solution, thus adding a small amount of OH^- will drastically change the rate of dissolution. To promote dissolution rate, the amount of OH^- needed is less than 2.0 eq/dm³ coal fly ash. The second step is the condensation or gelation reaction where silicate ions and aluminate ions begin to react at around 373 K which results in the concentration of Al^{3+}

dissolved in the alkali solution decreasing by formation of gel at period (b) shown in Fig. 2. As the reaction proceeds, aluminosilicate gel rapidly begins to deposit on the surface of the particle like a big flake which then transforms into a zeolite crystal. The concentration of Na⁺ in the alkali solution influences the rate of crystallisation which occurs before temperature reaches 393 K and continues for about 2 hrs at this temperature as is indicated in Fig. 2 (c). As gelation and zeolite crystallisation progress, aluminosilicate covers the surface of the fly ash and Al³⁺ concentration substantially diminishes resulting in the rate of zeolite crystallisation becoming slow after the consumption of all dissolved aluminate to form aluminosilicate. When the alkaline solution contains both Na⁺ and K⁺, zeolites containing large amounts of K⁺ are synthesised. However, zeolites containing Na⁺ are synthesised first and then they change to K⁺-type in an alkaline solution during of a series of zeolites synthesis reactions. As a result of this, K⁺-type zeolites are usually produced in an alkali solution containing both Na⁺ and K⁺.



Figure 2: Proposed mechanism for zeolite synthesis from coal fly ash (Murayama et al., 2002)

Various methodologies have been proposed, keeping in mind the end goal to get pure zeolite from coal fly ash synthesis rather than a mixture of zeolites (Izidoro et al., 2013). For instance, a fusion step before a hydrothermal treatment can make alkali extraction of more silicates and aluminates from ashes, increasing the yield of pure zeolites (Wang et al., 2008). However, the formation of a specific zeolite emphatically relies upon the proportion of SiO₂/Al₂O₃ in the starting material for hydrothermal reaction. The synthesis of zeolites is described with a complex mechanism, which includes the dissolution of Al and Si from fly ash, precipitation of aluminosilicate gel on undissolved fly ash particles, nucleation, development of crystalline

zeolites and cation exchangers (Shomkova and Stoyanova, 2016). Some of these procedures go on at the same time. However, they are influenced oppositely by treatment conditions. In this manner, the quality and the yield of the zeolites delivered is firmly reliant on the selection of the reaction parameters, as demonstrated by Querol and co-workers, 1999 who obtained 13 distinct zeolites utilizing the same fly ash, by varying the activation conditions. Unburnt material interferes with the synthesis of zeolites since they are deposited on the surface of ashes. This keeps them unchanged and diminishes the cation exchange capacity limit of the synthesised zeolite. Thus, unburnt carbon must be occasionally removed.

Park and others, 2000 suggested that, dry or molten-salt conversion method was mainly to prevent production of wastewater during the synthesis of zeolites. Salt mixtures were used instead of aqueous solution as reaction medium. The main drawback of this method was the production of only low CEC zeolites against the high temperatures used for the activation process. A two stage synthetic method where high silicon solutions were obtained from light alkaline attack of fly ash has also been reported. This enabled the synthesis of zeolites which were > 99 % pure (Hollman et al., 1999). In addition, the solid residue which results from this attack could be converted to classic zeolites by using conventional conversion methods. The major advantage of this process is that, it the produces pure zeolites instead of a mixture of zeolites or residual fly ash particles. High volume zeolites such as zeolites X and A may also be obtained from this method. Zeolites with high Al^{3+}/Si^{4+} ratio account for high ion exchange potential particularly for heavy metal and ammonium ions.

The traditional direct conversion method was optimised by Shigemoto et al., 1992 by the introduction of a fusion step prior to synthesis. This afforded distinct types of zeolites with potential industrial application such as NaP1, chabazite and herschelite. The direct conversion strategy was additionally applied by the utilization of dry conversion systems (Juan et al., 2001). The zeolitic materials acquired by direct conversion method have generally low CEC values because of incomplete conversion of the fly ash in zeolite. Hollman and others, 1999, reported on the synthesis of zeolites using SiO₂ extracts from coal fly ash getting high purity zeolites (>95% for Na-Pl and Na-X), and Moreno co-workers, 2002 enhanced this technique combining in the same procedure zeolites with high purity SiO₂ extracts and another zeolitic products obtained by direct conversion method.

Synthetic solutions are used under laboratory conditions to test the uptake of heavy metals (Moreno et al., 2002). It has been proven that there is competition between cations in the solutions to occupy exchangeable places in zeolites. This implies that the matrix effect of the solution has got great influence on the pollutant uptake efficiencies by zeolites. The presence of high Fe^{3+} or Ca^{2+} in solutions considerably reduces the uptake of other cations especially ammonium (Wang and Peng, 2010). Moreno and others, 2001, tested heavy metal uptake capacity from acid mine waters of zeolitic materials synthesised from coal fly ash with zeolite doses from 5 to 40 g L^{-1} depending on the type of zeolite and water matrix (Moreno et al, 2002). The results showed that the purification of pyrite mining wastewaters may be done effectively and efficiently by a direct cation exchange treatment using small amounts of zeolites. The tentative order of affinity of different ions to zeolite exchange sites followed the order: Fe^{3+} > $Al^{3+} > Cu^{2+} > Pb^{2+} > Cd^{2+} > Tl^+ > Zn^{2+} > Mn^{2+} > Ca^{2+} = Sr^{2+} > Mg^{2+}$. It was also demonstrated that NaPI and 4A zeolites have higher affinity for the other metal ions than for Ca^{2+} and Mg^{2+} . When solutions containing about 600 mg L⁻¹ of heavy metal cations and 800 mgL⁻¹ of calcium were treated with zeolites, the heavy metal cation concentration fell to $< 0.5 \text{ mgL}^{-1}$ whilst calcium concentration was still present in high concentrations.

The capacity of zeolites to adsorb heavy metals in wastewater was also investigated by Grigorios and co-workers, 2015. In the adsorption tests, aqueous solution of 1000 mg/L each of Cr, Cu, Ni, Pb, and Zn and 20 mg/L Cd were prepared. The precipitation potential of the different heavy metals was initially tested without utilizing any sort of solid adsorbent and there was no decrease in the concentration of the heavy metals after leaving them at 20^oC for 48 hours.

Further studies were done to test for the removal of zinc and cadmium ions from water in both single-and binary ion systems on synthetic pure zeolites (Izidoro et al., 2013). Izidoro and others, 2013, investigated the impact of competitive cations in binary ion adsorption by varying the initial concentration of one metal ion while that of the competitor ion remained unchanged. The outcome demonstrated that the adsorption rates in the binary ion system were lower than those in single ion system because of the competition between Cd^{2+} and Zn^{2+} ions to occupy exchangeable sites in the zeolites. At a fixed Zn^{2+} concentration, adsorption of Cd^{2+} and Zn^{2+} concentration.

concentration. The total metal ion adsorption percentages (AdTot %) additionally demonstrated a diminishing pattern at higher metal concentration.

Zeolites are also used in the immobilization of heavy metals in contaminated soils (Lin et al, 1998). This is very important as it avoids leaching of heavy metals and probably ground water pollution. Several experiments with zeolites synthesised from fly ash varying doses from 15 to 54 tons per hectare have been reported. Zeolites were mixed manually and applied by mixing the soil and the powder and a control was set where there was no addition of zeolites. This enabled the comparison of the reduction in heavy metal leaching with other fields. Sampling was done twice in two years after zeolite addition and the primary results showed that application of zeolites greatly reduced the leaching of elements such as Cd, Co, Cu, Ni and Zn. Ion exchange contributed to most of the reduction of leachable proportions. However, precipitation of insoluble phases as a result of pH rise from 3.3 to 7.6 induced by zeolite addition also contributed to the immobilisation of the pollutants. Lin and co-wokers, 1998, also did similar studies, but, mainly concentrated on immobilization of Cd in contaminated soils. The results were interesting as there was reduction from 88% Cd to 1% leachable contents through addition of synthetic zeolites to polluted soils with a dose of 16% wt.

Although synthetic zeolites have effectively been utilized as a part of water purification, they just effectively remove one type of water contaminants, which are metal cations. Water, however, contains a variety of contaminants which can be classified as physical, chemical, biological and radiological which come from different sources which includes chemical industries, metal plating operations and agricultural lands (Stanely, 2001). These contaminants are chlorinated hydrocarbons, heavy metals, saline water, bacteria specifically coliforms and general municipal and industrial waste. Zeolites can be modified with other chemicals so that they can remove more than one type of contaminant. Of particular interest are ZnO nanorods. As a semiconductor ZnO has gained much interest because of its photo-catalytic properties which are almost the same as TiO₂. Ismail and others, 2016, studied the morphological structures of ZnO nanostructures and found out that ZnO nanorods have porous holes on their surface which are believed to increase their surface area. They also have an average diameter of 250 nm and thickness of 500 nm while ZnO nanoflakes have an average diameter of 100 nm and thickness of 300 nm. As a result of these surface properties, zeolites modified with ZnO nanorods are expected to have better efficiency in water purification.

Most researchers have focused on the development of materials which can effectively harvest solar irradiation and utilise it for green environmental pollution management. This is due to the abundance of solar energy, which has been reported that the amount striking the earth in an hour is higher than the amount consumed in the entire year (Lewis, 2007). This has made photocatalysis interesting because it uses the renewable solar energy to activate the oxidation and reduction processes responsible for the removal of persistent and toxic organic compounds, and microorganisms in water. Several kinds of photo-catalytic metal oxides, such as titanium dioxide (TiO₂), zinc oxide (ZnO), iron (III) oxide (Fe₂O₃), zirconia (ZrO₂), tungsten trioxide (WO₃) and tantalum pentaoxide (Ta₂O₅) have been applied for effective photo-degradation of various harmful organic pollutants in water as well as antibacterial characteristics (Alessandro, 2017). Table 2 shows the values of band gaps of the above mentioned semiconductors.

Semiconductor	Eg (eV)
Si	1.1
Fe ₂ O ₃	2.3
CdS	2.5
WO ₃	2.8
TiO ₂ (rutile)	3.0
TiO ₂ (anatase)	3.2
ZnO	3.2
SnO ₂	3.5

Table 2: Forbiden bandwidths of some popular semiconductors (Sobczynski and Dobosz, 2001)

ZnO has a variety of applications in spintronic, magneto-optical devices, photo-catalysis, solar cells, gas sensors and light-emitting diodes fabrication due to its electronic and optical properties (Batistela et al., 2017; Mohamed and Abu-Dief, 2018). It has also emerged as a promising candidate for environmental application because of its direct and wider band gap energy in the near-UV spectral region, strong oxidation ability, a great photolytic property and large free-exciton binding energy so that exciton emission process can exist at or above room temperature (Alesandro,2016). ZnO exists as hexagonal wurtizite, cubic zinc blend and cubic rock salt structures. The hexagonal wurtizite ZnO possesses good adsorption properties towards heavy metals. It has been reported that ZnO has good efficiency, chemical stability

and high surface area (Ibrahim, 2017). In addition, it's non-toxic, easily available and cheap. The semiconductor properties make ZnO a catalyst for degradation of several recalcitrant substances by using heterogeneous photo-catalysis. Upon absorption of UV/Vis radiation ZnO promotes the formation of highly oxidising species such as 'OH and O_2 .'' radicals that degrades organic pollutants (Batistela et al., 2017; Mohamed and Abu-Dief, 2018). The absorption process is dependent on parameters such as pH, temperature, catalyst stability and substrate concentration. The ZnO is an environmentally friendly material as it is compatible with living organisms thus lending itself nicely to a broad range of daily applications that will not leave any risks to human health, and environmental impact (Alesendro, 2017; Mohamed and Abu-Dief, 2018).

ZnO has the same band gap as TiO₂ (~3eV), large excitation energy (60meV) and deep violet/ borderline ultraviolet absorption at room temperature and for these reason it is expected to have a similar photocatalytic efficiency as TiO₂. ZnO has been proposed as an alternative to TiO₂ as it possesses same band gap energy, but exhibits higher absorption efficiency across a large fraction of the solar spectrum when compared to TiO₂ (Ong et al, 2018). Fenoll and others, 2011, also evaluated the photosensitization of ZnO and TiO₂ by comparing the photo degradation of fungicides in leachate water under solar irradiation and found out that ZnO is a better photo-catalyst compared to TiO₂ under solar irradiation. In addition, ZnO has antifouling and antibacterial properties (Ruchi et al., 2017). Furthermore, Liang and co-workers, 2016, reported that the production cost of ZnO is up to 75% lower than that of TiO₂ and Al₂O₃ nanoparticles, thus can substitute TiO₂ which is uneconomical for large scale water treatment operations (Alesandro, 2017). The heterogeneous photo-catalytic steps can be summarised as shown in the diagram below (Herrmann et al., 1999).

- 1. The organic contaminants diffuse from the liquid phase to the surface of ZnO
- 2. Adsorption of the organic pollutant on the surface of ZnO.
- 3. Oxidation and reduction in the adsorbed phase
- 4. Desorption of the products
- 5. Removal of the products from the interface region



Figure 3: Heterogeneous photocatalytic oxidation steps. Adapted from (Hermann et al, 1999)

The mechanism for photocatalytic discoloration is believed to be as that represented in Fig. 3 (Rauf and Ashraf, 2009). When the catalyst is exposed to solar irradiation, electrons are promoted from the valance band to the conduction band producing an electron-hole pair [equation 2]. The electron-hole pairs can migrate to the ZnO surface and be involved in a series of redox reactions as shown in [equations 3-5] where the H⁺ reacts with water and hydroxide ions to produce hydroxyl radicals while e⁻ reacts with O₂ to produce superoxide radical anions then hydrogen peroxide [equation 6]. The hydrogen peroxide and superoxide radical will react together to form hydroxyl radicals [equations 8-10]. Then the resulting hydroxyl radical will attack the pollutants which will be adsorbed on the surface of ZnO catalyst to rapidly produce intermediate compounds. The intermediates will later be converted to green compounds such as CO₂, H₂O and mineral acids as shown in [equation 12] (Rauf and Ashraf, 2009; Ong et al., 2017).

$$ZnO \xrightarrow{HV} ZnO (h_{(VB)}^{+}) \dots \dots (2)$$

$$ZnO (h_{(VB)}^{+}) + H_2O \rightarrow ZnO + H^{+} + OH^{\bullet} \dots (3)$$

$$ZnO (h_{(VB)}^{+}) + OH^{-} \rightarrow ZnO + OH^{\bullet} \dots (4)$$

$$ZnO (e_{(CB)}^{-} + O_2 \rightarrow ZnO + O_2 \bullet^{-} \dots (5)$$

$$O_2 \bullet^{-} + H^{+} \rightarrow HO_2^{\bullet} \dots (6)$$

$$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \dots (7)$$

$$ZnO (e_{(CB)}^{-}) + H_2O_2 \rightarrow OH^{\bullet} + OH^{-} \dots (8)$$

$$H_2O_2 + O_2 \bullet^{-} \rightarrow OH^{\bullet} + OH^{-} + O_2 \dots (9)$$

$$H_2O_2 + hv \rightarrow 2OH^{\bullet} \dots (10)$$

....

Organic Pollutant + 0	$H^{\bullet} \rightarrow Intermediates \dots \dots$	(11)
Intermediates $\rightarrow CO_2$	$+ H_2 0 \dots $	(12)

A schematic presentation of the mechanism of generation of the oxidative species in a photocatalytic study is shown in figure 4.



Figure 4: Schematic diagram showing generation of oxidative species in the photocatalytic study

The efficiency of ZnO is limited because of its low adsorption capability (small active area) and the possibility of photo-corrosion. Even though the use of ZnO nano particles with broad surface area can improve their photo-activity, nanoparticles of ZnO are difficult to recover at the end of the process. To overcome this problem, ZnO nanoparticles can be supported on an inert or active material such as zeolite to improve their adsorption and consequently the catalyst efficiency (Batistela et al., 2016).

In this project ZnO nanorods are of interest because they have large surface area compared to other ZnO nano particles like ZnO nanoflakes, ZnO nanowires, ZnO nanofibers etc. According to Alessandro and co-workers, 2017, ZnO has become known as a promising candidate for environmental application because it possesses a direct and wide band gap energy in the near-UV spectral region, a strong oxidation ability and great photocatalytic property as well as large free exciton binding energy so that exciton emission processes can persist at or even above room temperature. The ZnO grows easily and its thermodynamically stable phase is the hexagonal wurtzite structure. It is also environmentally friendly and compatible with living organisms which fits it perfectly in water purification. The band gap of ZnO is \sim 3 eV, which is similar to that of TiO₂ and thus the two are expected to have similar photo-catalytic properties

(Alessando et al., 2017). ZnO is also relatively cheap compared to TiO_2 thus the usage of TiO_2 is uneconomical for large scale water processes.

1.8 Dissertation Outline

This dissertation comprises of six chapters. The first chapter is made up of introduction and literature review. The introduction comprises of brief background information, main aim and objectives. Literature review focuses on the chemistry of zeolites and metal oxides mainly ZnO, previous work on their synthesis, use as adsorbent and photo-catalyst and some of the modifications carried out on these materials.

Chapter two comprises of the research methodology, materials and procedures carried out to achieve the objectives of this dissertation. It gives a list of the chemical reagents used in the study and detailed procedures on the synthesis of zeolites and their modification. It also includes the water analysis procedures for adsorption and photo degradation using the synthesised modified zeolites.

Chapter three has characterisation results from FT-IR, BET, XRD, TGA and SEM-EDX. In addition, results from the analysis and evaluation of water are presented including the adsorption isotherms and kinetic studies. Chapter four presents the discussion and interpretation of the results obtained from chapter three.

Chapter five and six gives the general conclusion and recommendations for future work respectively. And finally, is the list of references.

2.1 Research Methodology

The research methodology is summarised in Fig. 5. The first step involved the synthesis of zeolites from coal fly ash (CFA) using a modified hydrothermal method by (Chigondo et al., 2013). The second step was the synthesis of porous shell of ZnO on the zeolite prepared from above (Ruchi et al., 2016).



Figure 5: Research methodology outline

This was followed by growing of ZnO nanorods and ZnO nanoflakes on the seeded zeolite Ismail, 2015. The synthesised materials were characterised using FT-IR, BET, XRD, TGA and SEM-EDS. The adsorption experiments were carried out using the batch method. The analysis of heavy metals (Pb²⁺ and Cd²⁺) and methylene blue dye was done using Flame atomic absorption spectrometer and UV-Vis spectroscopy respectively at the University of Zimbabwe Chemistry department. All the sorption studies were done using a mechanical shaker. For, UV degradation and photo-catalysis a magnetic stirrer was used to stir up the mixture and increase the rate of catalysis. Kinetic studies were done on both the heavy metals and methylene blue dye using Ze-ZnO nanorods and Ze-ZnO nanoflakes. For the sorption isotherms, the experiment was done while varying adsobant (Ze-ZnO nanorods) dosage for the heavy metals and varying initial concentration for the methylene blue dye degradation.

2.2 Materials and Procedures

2.2.1 Materials

The following materials and reagents were used in this study: Coal fly ash was obtained from Coca Cola Company in Zimbabwe.

Zinc acetate dihydrate (C₄H₆O₄Zn.2H₂O) (98%, Associated chemical enterprises), methanolic solution of KOH (85%, Merck), n-butanol (A.R grade), methanol (A.R grade, Merck), zinc nitrate [Zn (NO₃)₂6H₂O] (98% purity, Glassworld), hexamethylenetetramine C₆H₁₂N₄ (99%, Sigma- Aldrich), deionised water, chloroform (A.R grade, Merck), cadmium chloride (CdCl₂. H₂O) (98%, Merck), lead nitrate [Pb(NO₃)₂] (99%, HiMedia Laboratories), sodium hydroxide (98%, Skylabs) and silicon oil.

2.2.2 Procedures

2.2.2.1 Sampling and pre-treatment of coal fly ash.

The coal fly ash was obtained from the Coca Cola Company of Zimbabwe. The sample was oven dried at 50° C and before use, it was screened by a 180-micron sieve, followed by removal of magnetic materials mainly iron fillings using a magnet. The magnetic particles had to be removed first because they interfere with zeolite formation (Chingondo et al., 2013)

2.2.2.2 Synthesis of Zeolites

Zeolites were synthesised using a hydrothermal method with coal fly ash the main feedstock following a procedure reported in literature (Chigondo and co-workers, 2013). In a typical experiment, 7.60 g of coal fly ash were added to a 250 mL beaker containing 70 cm³ of 3 M NaOH. The resulting solution was heated at 100° C for 24 hr. The formed zeolite was washed several times with distilled water until pH of 10 is attained. The obtained zeolite was dried to a constant mass at 100° C and stored in a desiccator before use.

2.2.2.3 Synthesis of porous shell of ZnO

In the preparation of porous shell of ZnO, 0.27 g of zinc acetate dihydrate was dissolved in 125 mL of methanol under vigorous stirring at 60° C. In a separate flask, KOH, (1.68 g) was dissolved in 100 mL of methanol. Subsequently, 65 mL of the methanolic solution was added to the zinc acetate solution dropwise for 15 mins at 60° C. The reaction mixture was stirred for 2 hr 30 mins at 60° C. After the reaction, the mixture was cooled, washed with methanol and centrifuged. A 70 ml portion of N-butanol, 5 mL of chloroform and 5 mL of methanol were added to disperse the precipitate. A 1 g sample of the zeolite was added to the solution and stirred overnight. The seeded zeolite powder was obtained with seed particles on the surface by filtering and the material was annealed at 350° C for 30 mins.

2.2.2.4 Growing ZnO nanorods ZnO and nanoflakes on the seeded zeolite

Following a procedure by Ismail, 2015, 14.97 g of zinc nitrate and 7.00 g of hexamethylendiamine were dissolved in 500 mL of deionized water. A 13.9 g of the seeded zeolite was added to the final solution (1/3 of the sample was set aside for the synthesis of nanoflakes) while stirring for 4 hrs without heating to obtain a homogenous solution. The solution was put in a schott bottle and immersed in a water bath at 95° C for the growth process. The immersed sample was washed several times through Buchner filtration to remove unwanted particles and dried for 10 mins at 150° C. After drying, the sample was annealed at 500° C for 1hr. For the growth of nanoflakes, 1/3 of the sample which was set aside was stirred for 4hrs with heating at 60° C until a homogenous mixture was obtained. The solution was put in a schott bottle and immersed in a 95°C for the growth process.

sample was washed several times through Buchner filtration to remove unwanted particles and dried for 10 mins at 150°C. After drying, the sample was annealed at 500°C for 1 hr.

2.2.3 Characterization of zeolitic materials

Characterization was done using Fourier transform infrared spectroscopy (FT-IR), Brunauer Emmett Teller (BET) surface area analysis, Scanning electron microscopy (SEM), X-ray diffraction (XRD), Thermogravimetric analysis (TGA) and Energy Dispersive X-ray Spectroscopy (EDS).

2.2.3.1 Fourier transform infrared (FT-IR) spectroscopy

Fourier transform infrared spectroscopy is a technique based on the excitation of molecular vibrations by light absorption. It is commonly used in the determination of structure in organic and inorganic bonds by identifying the functional groups present in a sample.

It utilizes an ingenious device called a Michelson interferometer for making precise measurements of the electromagnetic radiation. When infrared radiation passes through the sample, some is absorbed by the sample and some is transmitted. The resulting spectrum corresponds to the molecular absorption and transmission, which is specific for that sample. This means that each and every molecule will have a spectra specific to itself only.

The sample analysis process entails the emission of infrared radiation from a black body source. The beam of radiation passes through an aperture which regulates the amount of energy reaching the sample and ultimately to the detector. The beam enters the interferometer where the spectral encoding takes place. The interferogram produced represents the signal which then exits the interferometer. The radiation beam enters the sample compartment where it is transmitted or reflected off the surface of the sample, depending on the type of analysis being carried out. This is where specific frequencies of energy, uniquely characteristic of the sample, are absorbed. The beam finally passes through to the detector for the final measurement to be taken. The detectors used are specifically designed to measure the special interferogram signal. FT-IR spectroscopy was used in this study to characterize the coal fly ash and the zeolitic materials.

2.2.3.2 Brunauer Emmett Teller (BET) surface area analysis

The BET technique was named after S. Brunauer, P. H. Emmet and E. Teller. The method is applied in the analysis of pharmaceuticals, catalysts, projectile propellants, medical implants, filters, cements and adsorbents. The BET method is based on the adsorption of gas on a surface. Adsorption is a consequence of surface energy change. The energy is kept very low in the bulk when every atom or molecule is surrounded by neighbours. The amount of the adsorbed gas at a given pressure allows for the determination of surface area. Hence, BET was used to determine the surface area of the different zeolitic materials synthesized.

2.2.3.3 Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) is a type of electron microscopy that produces images of the sample's surface by scanning it with a high energy beam of electrons in a raster scan pattern. The signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity is produced when electrons interact with the atoms that make up the sample.

In this project, SEM was used to obtain the morphology of the different zeolitic materials synthesized.

2.2.3.4 X-ray diffraction (XRD)

X-ray diffraction is a unique method used for determination of crystallinity of a compound. It is primarily used for ID of crystalline material, ID of different polymorphic forms, distinguishing between armorphus and crystalline material and quantification of the percent crystallinity of a sample. XRD is based on constructive interference of monochromatic X-rays and crystalline sample. X-rays of a known wavelength are passed through a sample and the interaction of the incident rays with the sample produces constructive interferences when conditions satisfy Bragg's Law ($n\lambda = 2d \sin\theta$). This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. Energy dispersive X-ray Spectroscopy is a qualitative and quantitative X-ray microanalytical technique that provides information on the chemical composition of the sample for elements with atomic number (Z)> 3.

The energy of the incoming X-ray is dissipated by the creation of a series of electron hole pairs in the semiconductor crystal. A high bias voltage is applied across the crystal and this causes electrons and holes to move to electrodes on opposite sides of the crystal, producing a charge signal which is passed to the pulse processor. The size of the signal is proportional to the energy of the incoming X-ray. For a silicon detector, ~3.8 eV is used to generate each electron-hole pair (~2.9 eV for Ge). So for an incoming Ni K α X-ray of energy 7.477 keV, 1968 electronhole pairs will be produced, and for an Al K α X-ray of 1.487 keV, 391 electron-hole pairs will be generated. By measuring the amount of current produced by each X-ray photon, the original energy of the X-ray can be calculated. An EDS spectrum is essentially a histogram of the number of X-rays measured at each energy.

2.2.3.6 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) is a method of thermal analysis in which changes in physical and chemical properties of materials are measured as a function of increasing temperature (with constant heating rate), or as a function of time (with constant temperature or constant mass loss). Measurements are primarily used to predict thermal stability of products. The breaking and formation of chemical bonds at elevated temperatures leads to changes in the weight of the sample which is monitored by a very sensitive analytical balance. Changes in mass of a sample due to various thermal events (desorption, absorption, sublimation, vaporization, oxidation, reduction and decomposition) are studied while the sample is subjected to a program of temperature change. Therefore, it is used in the analysis of volatile products, gaseous products lost during reaction in thermoplastics, thermosets, elastomers, composites, films, fibers, coatings and paints.

The instrument used for TGA analysis is a programmed precision balance for a rise in temperature called a thermobalance. The thermobalance consists of an electronic microbalance, a furnace, a temperature programmer and a recorder. During analysis, the samples are placed in crucible that is positioned in a furnace on a quartz beam attached to an automatic balance

and the weight of sample is continuously recorded as the temperature increases. The horizontal quartz beam is maintained in the null position by the current flowing through the transducer coil of an electromagnetic balance. A pair of photosensitive diodes acts as a position sensor to determine the movement of the beam. Any change in the weight of the sample causes a deflection of the beam, which is sensed by one of the photodiodes. The beam is then restored to the original null position by a feedback current sent from the photodiodes to the coil of the balance. The feedback current is proportional to the change in weight of the sample (Willard, et al, 1988). In this work, TGA was used to determine the stability of the zeolitic materials synthesized.

2.2.4 Adsorption experiments

All adsorption experiments were carried out using the batch method. This was done by agitating a given dose of each adsorbent in a synthetic solution of each model pollutant in deionised water. A 0.2 g of adsorbent was dispersed in a 50 mL of the synthetic solution at room temperature. The mixtures were placed on a shaker and agitated for 60 minutes. The adsorbent was separated by filtering, and the concentration of each heavy metal in the filtrate determined by flame atomic absorption spectroscopy (FAAS). All assays were carried out in triplicates and the average values taken.

2.2.4.1 Kinetic Studies

In order to assess the rate of adsorption for heavy metals and methylene blue dye, experiments were carried out under the following conditions: For heavy metals, the amount of adsorbent (Ze-ZnO nanorods) used was 0.2 g per 50 mL of solution; the initial metal concentration for both Cd²⁺ and Pb²⁺ was 300 ppm; the shaking time was 120 minutes. Aliquots of sample were withdrawn at 30-minute intervals and the concentration of each heavy metal was determined by FAAS. The adsorption kinetic studies were carried out separately for each heavy metal ion. The temperature of the mixtures was maintained at room temperature. For methlylene blue dye, the amount of adsorbent (Ze-ZnO nanorods) was 0.2 g per 50 mL of solution; the initial dye concentration was 75 ppm; the shaking time was 6 hrs. Aliquots of sample were taken at 30-minute intervals and the concentration of the dye was determined by UV-Vis spectroscopy.

2.2.4.2 Isotherms Studies

The conditions used to generate adsorption isotherms were as follows: For heavy metals, the adsorbent dosage ranges were 0.10 g, 0.15 g, 0.2 g and 0,25 g; the initial concentration for Pb²⁺ and Cd²⁺ were 300ppm; the shaking time 6 hrs. Aliquots were taken after 2 hrs for measurements with FAAS. The adsorption isotherms were carried out separately for each heavy metal ion. The adsorption experiments were carried out at room temperature. For methylene blue dye, the adsorbent dosage was 0.2 g; the initial dye concentrations were 5 ppm, 25 ppm, 50 ppm and 75 ppm; the mixtures were exposed to solar irradiation 6 hrs. Aliquots where taken after 6 hrs and the remaining dye concentrations were measured with UV-Vis spectroscopy.

2.2.5 Preparation of Stock Solutions

The stock metal solutions of 1000 ppm concentrations were prepared from metal salts as follows:

2.2.5.1 Cadmium Stock Solution

A 1000 ppm stock solution of Cd^{2+} was prepared by dissolving 1.79 g of cadmium chloride in 250 mL of deionised water using a 1000 mL volumetric flask. The working standards for FAAS analysis were in the range 0.25-2.0 ppm.

2.2.5.2 Lead Stock Solution

A 1000 ppm stock solution of Pb²⁺ was prepared by dissolving 1.60 g of lead nitrate in 250 mL of deionised water using a 1000 mL volumetric flask and diluting to 1 L. The working standards for FAAS analysis were in the range 2.0-20 ppm.

2.2.5.3 Methylene Blue Stock Solution

A 75 ppm stock solution of methylene blue dye was prepared by dissolving 0.04 g of the dye in a 500 mL of water in a volumetric flask. The working standards for UV/Vis analysis were 2.0-5.0 ppm.

2.2.6 Analysis and evaluation (application)

Analysis of heavy metals which are Lead (Pb) and Cadmium (Cd) was done using Atomic Absorption Spectrometer (AAS) and an organic pollutant (methylene blue dye) was analysed using UV/Vis spectroscopy.

2.2.6.1 Flame Atomic Absorption Spectroscopy (FAAS)

It was developed by Walsh IN 1995 and now is the most widely used technique for elemental analysis. Electrons are excited from ground state to a higher energy level by irradiating an atom with radiation whose wavelength is given by equation 13:

Provided certain selection rules are satisfied. The sample is introduced as an aerosol into the flame, where the analyte ions are converted into free atoms according to equation 14:

Once formed, the free atoms absorb radiation of specific wavelength from the external source hallow cathode lamp and the amount of radiation is detected and determined by FAAS. For monochromatic radiation, absorbance, A, is directly proportional to the path length, b, through the medium, and the concentration, c, of the absorbing species. This is presented by equation 15.

The work on adsorption of heavy metals was done using flame atomic adsorption spectroscopy. The instrument conditions used are as follows:

Experimental conditions for the FAAS

Spectrometer	Shimadzu AA-6701F
Lamp	Hamamatsu photonics
Fuel gas	H_2C_2
Flow rate (L/min)	1.8 1.8
Element	Pb Cd
Wavelength nm	324.8 228.8
Lamp Current (mA)	10 5
Slight width (nm)	0.5 0.5

2.2.6.2 UV-Vis Spectroscopy

An ultraviolet-visible (UV/Vis) spectrophotometer consists of three components: the source, the dispersive system (combined in a monochromator) and a detector. These components are typically integrated into the same instrument to make spectrophotometers for chemical analysis. The sample to be analysed can be placed in the optical path before or after dispersive system and recorded spectra can be treated by using a number of different computer algorithms. This technique is widely used for analytes that are capable of absorbing UV-Vis radiation.

The light sources commonly used in this spectral domain are of two types. An incandescent lamp made from a tungsten filament housed in a glass envelope is used for the visible portion of the spectrum, for wavelengths longer than 350 nm. For the UV portion (wavelengths shorter than 350 nm), a medium pressure deuterium arc lamp is used. Detectors are again of two types: photomultiplier tubes and semiconductors (e.g. silicone photodiodes and charge transfer devices).

Double-beam spectrophotometers allow different measurements to be made between the sample and the analytical blank. UV-Vis spectroscopy uses light in the visible and near ultraviolet as well as near infra-red ranges. Absorption in the visible region results in molecules undergoing electronic transitions. The absorbance is measured and the concentration of the

analyte is related to the signal by the Beer-Lambert law as shown in equation 15. For the evaluation of methylene blue dye UV-Vis spectroscopy was utilised.

3.1 Characterisation results

3.1.1 FT-IR results

Coal fly ash and the synthesised zeolites, zeolites seeded with ZnO porous shell, Ze-ZnO nanorods and Ze-ZnO nanoflakes were analysised using a PerkinElmer FTIR and the spectra obtained are presented in figure 6.



Figure 6: Spectra of (a) CFA, (b) Zeolites, (c) Ze-ZnO NR, (d) Ze-ZnO NF and (e) ZnO seeded zeolites

3.1.2 BET results

Coal fly ash and the synthesised zeolites, zeolites seeded with ZnO porous shell, Ze-ZnO nanorods and Ze-ZnO nanoflakes were taken for analysis using BET TriStar II 30120 V1.02, and values of the surface are area represented in table 3 below.

Table 3: Difference in the Pore diameter, Pore volume and BET surface area for the Zeolite, ZnO seeded zeolite, Ze-ZnO nanorods and Ze-ZnO nanoflakes

	Pore diameter	Pore volume	Specific surface	BET Surface
	nm	cm ³ /g	area m²/g	area m²/g
Zeolite	22.7427	0.030709	8.5596	8.8332
ZnO seeded	25.3282	0.022320	6.6092	6.7167
zeolite				
Ze-ZnO	24.942	0.175979	37.9699	39.0281
nanorods				
Ze-ZnO	19.7740	0.177775	39.4559	40.6632
nanoflakes				

3.1.3 SEM results

Coal fly ash and the synthesised zeolites, zeolites seeded with ZnO porous shell, Ze-ZnO nanorods and Ze-ZnO nanoflakes were taken for analysis using SEM JOEL-JSM 7500F) and the SEM images are represented in figure 7.





Figure 7: Showing SEM images of the zeolites, Ze-ZnO NR, Ze-ZnO NF, ZnO seeded zeolites (a)-(d) at 20 µm respectively and (e)-(h) at 2 µm of zeolites, Ze-ZnO NR, Ze-ZnO NF, ZnO seeded zeolites respectively

3.1.4 XRD results

Zeolites, Ze-ZnO nanorodes and Ze-ZnO nanoflakes were taken for analysis using a Bruker-AXS D8 Advanced diffractometer and the patterns are represented in figure 8.



Figure 8: (a) shows the XRD pattern of zeolites (b) XRD pattern of Ze-ZnONR (c) XRD pattern of Ze-ZnNF

3.1.5 EDS results

Zeolites, Ze-ZnO nanoflakes, Ze-ZnO nanorods and ZnO seeded zeolites were taken for analysis using an EDX-700HS and the spectrum are represented in figure 9.





Figure 9: Shows the EDS spectra for (a) zeolite (b) Ze-ZnONR (c) Ze-ZnONF and (d) ZnO seeded Zeolite



3.1.6 TGA results

Figure 10: TGA curves of (a) Ze-ZnO NR (b) Zeolites (c) CFA (d) Ze- ZnO NF and (e) ZnO seeded zeolites

3.2 Analysis and Evaluation Results of Heavy metals

3.2.1 Heavy metal uptake, Comparison of Ze-ZnO nanorods and Ze-ZnO nanoflakes

Table 4 shows the initial and final concentration of Pb^{2+} and Cd^{2+} after purification with Ze-ZnO nanorods and Ze-ZnO nanoflakes. The adsorbent dosage for both was 0.2 g and the mixture was allowed to shake for 60 minutes under room temperature and then taken for analysis on the FAAS Shimadzu 6701F.

Table 4: Concentration (ppm) of the two heavy metals in the tested aqueous solutions after adsorption with 0.2 g of the adsorbent

		Zeolites Modified	Zeolites Modified with ZnO nanoparticles		
Metal	Initial	Ze-ZnO NR	Ze-ZnO NF		
Pb ²⁺	300	49.9828	4.289025		
\mathbf{Cd}^{2+}	300	254.745	237.7825		

3.2.2 Adsorption studies

Figure 11-14 shows results for adsorption studies by varying amounts of the Ze-ZnO nanorods from 0.1 g to 0.25 g. The initial concentration of the heavy metal was 300 ppm and mixture was allowed to shake for 60 minutes at room temperature and pressure.



Figure 11: Showing the effect of adsorbent (Ze-ZnO Nanorods) dosage on heavy metal adsorption



Figure 12: showing the Langmuir adsorption isotherm for Pb^{2+} and Cd^{2+}



Figure 13: Showing the linear plots of the Langmuir isotherm for Pb²⁺



Figure 14: Showing the linear plots of the Langmuir isotherm for Cd²⁺

3.2.3 Kinetic studies

Figures 15-16 show results for kinetic studies. It indicates the variation of adsorption capacity with time. The initial concentration of the heavy metal was 300 ppm and the dosage of Ze-ZnO nanorods was 0.2 g. The remaining concentration was measured at 30 mins interval and the adsorption was allowed to go on for 120 minutes at room temperature.



Figure 15: Adsorption capacity versus adsorption time of Pb^{2+} and Cd^{2+} on Ze-ZnO nanorods (initial metal concentration=300 ppm, adsorbent dosage= 0.2 g)



Figure 16: Pseudo-second order kinetics for the adsorption of Pb^{2+} and Cd^{2+}

3.3 Analysis and Evaluation of Methylene Blue Dye

3.3.1 Methylene Blue Dye UV degradation, Comparison of Ze-ZnO NR and Ze-ZnO NF

Figures 17 and 18 show the photocatalytic activities of Ze-ZnO nanorods and Ze-ZnO nanoflakes, photo degradation experiments were conducted using varying methylene blue dye concentration from 5 ppm to 75 ppm under UV irradiation for 6 hrs and measuring the remaining concentration using UV/Vis spectroscopy at 650 nm. The amount of adsorbent used was 0.2 g for all the experiments.



Figure 17: Remaining concentration after UV degradation



Figure 18: Degradation efficiencies of Ze-ZnO nanorods and Ze-ZnO nanoflakes

3.3.2 Photo catalysis using Ze-ZnO nanorods.

Figure 19 shows photocatalysis results of Ze-ZnO nanorods for 6 hrs expose in the sun and effect of increasing in dye concentration from 5ppm to 75 ppm. The amount of adsorbent used was 0.2 g.



Figure 19: Showing results of degradation efficiency as the initial concentration of methylene blue dye changes using Ze-ZnO nanorods for 6 hrs

3.3.3 Photo-decomposition of Methylene blue dye as a function of time

Figures 20 and 21 show the photo-degradation of methylene blue dye as a function of time when a solution containing Ze-ZnO nanorods and Ze-ZnO nanoflakes where exposed to solar irradiation for 6 hrs. The initial concentration of the methylene blue dye was 50ppm and the adsorbent dosage was 0.2 g.



Figure 20: Effect of time versus concentration on photo-decomposition using Ze-ZnO NR and Ze-ZnO NF



Figure 21: First-order kinetic plot of the Methylene blue dye decomposition on Ze-ZnO NR and Ze-ZnO NF

3.3.4 Kinetic Studies

Figures 22 and 23 shows that adsorption kinetics of methylene blue dye on Zn-ZnO nanorods is time dependant at an initial concentration of 75 ppm of dye and 0.2 g of the catalyst. The experiment was done for 5 hrs under exposure to solar irradiation.



Figure 22: showing adsorption capacity with adsorption time for the adsorption of methylene blue dye on Ze-ZnO nanorods(adsorbent dosage 0.2 g, Initial concentration 75 ppm)



Figure 23: Pseudo-second order kinetics for the adsorption of methylene blue dye on Ze-ZnO nanorods

3.3.5 Adsorption studies

Figure 24 and 25 shows the equilibrium adsorption isotherm for the adsorption of methylene blue dye on Ze-ZnO nanorods. This was done using 0.2 g of the adsorbent and varying the initial dye concentration and exposure to the sunlight for 6 hrs.



Figure 24: Adsorption isorthem for methylene blue dye on Ze-ZnO nanorods (adsorbent dosage 0.2 g, methylene blue concentration 5 ppm-75 ppm



Figure 25: Langmuir plot of methylene blue dye on Ze-ZnO nanorods

4.1 Characterisation Results

4.1.1 FT-IR analysis

Figure 6 shows FT-IR transmittance spectra for coal fly ash and synthetic zeolites, Ze-ZnO porous shell, Ze-ZnO nanorods and Ze-ZnO nanoflakes respectively in the range 0- 4500 cm⁻ ¹. There are several band shifts upon formation of zeolite from coal fly ash. The band at around 1000 cm⁻¹ in the FT-IR spectra of coal fly ash became sharper and shifted to a lower frequency around 900-980 cm⁻¹ in the spectra of the zeolitic materials. This confirms the development of double ring mode which is associated with zeolite cages and rings that is notably absent in the coal fly ash spectrum. These bands result from the Si-O and Al-O stretching onto the surface of zeolite and are in good agreement with the value reported in literature (Lin et al., 2018; Hildebrando et al., 2014). The absorption peaks between 3450 cm⁻¹ and 3550 cm⁻¹ and between 1500 cm⁻¹ and 1650 cm⁻¹ are assigned to O-H and O-H-O in the zeolite structure respectively (Mohamed and Abu-Dief, 2018; Li et al., 2018; Wang et al., 2014; Hildebrando et al., 2014). In the region within 500-420 cm⁻¹, related to the deformations of O–T-O bond, there is evidence for this band in all the zeolitic material between 420 cm⁻¹ and 500 cm⁻¹ (Chigondo et al., 2013). Hildebrando et al, 2014 also states that the peaks near 680cm-1 and 745 are assigned to T-O-T (T= Al or Si) vibrations of the zeolite framework. For all the samples modified with ZnO, a characteristic Zn-O stretching mode for wurtzite ZnO was found at wavenumbers between 400-500 cm⁻¹ (Hernandez-Carrillo et al., 2018). Stretching modes bellow 500 cm⁻¹ represents the successive formation of ZnO nanoparticles (Mohamed and Abu-Dief, 2018).

4.1.2 BET analysis

The BET surface area was 8.83, 6.72, 39.03 and 40.66 m²/g for zeolite, ZnO seeded zeolite, Ze-ZnO nanorods and Ze-ZnO nanoflakes respectively. The formation of the ZnO nanrods and ZnO nanoflakes results in an increase in the surface area and pore volume as shown in table 3. The specific surface area for the zeolites 8.56 m²/g is in agreement with 9.2 m²/g obtained by (Loila et al., 2012) and 11.2 m²/g (Batistela, 2017). This can be attributed to the compensation cation which affects pore opening by blocking it or keeping it available. Since sodium ion has

a small hydration radius, it can penetrate the pores of the zeolite blocking them. In the presence of larger cations such as calcium which possesses a larger hydration radius, it cannot penetrate the pores and remains preferably on the external surface of the zeolite increasing its surface area. The surface area of Ze-ZnO nanoflakes 40.6632 m²/g was small compared to those produced by (Ruchi et al., 2016) 382.882 m²/g. This can be attributed to the fact that different zeolite types where used in the modification process. The Ze-ZnO nanorods had a lower BET surface area compared to the Ze-ZnO nanoflakes.

4.1.3 SEM analysis

Morphological studies by SEM, shown in figure 7 indicate the formation of ZnO nanoflakes and ZnO nanorodes on the surface of zeolite. The morphology of the ZnO nanorods {Fig. 7 (b)} and ZnO nanoflake {Fig. 7(c)} on the zeolite surface shows that the presence of these nanostructures does not significantly affect the interaction of contaminants on the zeolite structure. The SEM images show that the core would be able to carry out its function even after the formation of the ZnO nanorods or nanoflakes shell. However, the ZnO nanorods seem to be densely packed compared to the ZnO nanoflakes and thus expect Ze-ZnO nanorods to have reduced the zeolite interface for adsorption characterisics compared to the Ze-ZnO nanoflakes. The image indicates that the Ze-ZnO nanoflakes has more surface are exposed for adsorption compared to the Ze-ZnO nanoflakes. This is clearly indicated in figures 7 (b) and (c).

4.1.4 XRD analysis

Figure 8 represents the XRD patterns of zeolites, Ze-ZnO nanorods and Ze-ZnO nanoflakes at 2θ ranging from 5° to 100°. There are three main characteristic peaks at 2θ : 13.59°, 23.71° and 27.38° in Fig. 8 (a) confirming a successful formation of zeolites. These values agreed with those found by (Aldahri et al., 2016) which were 12.46°, 21.96° and 28.10° respectively. The positions of the diffraction peaks corresponding to zeolites framework remains almost identical after modifying them with ZnO nanorods and ZnO nanoflakes indicating that the preparation methods do not change the crystal structure of zeolites. Moreover, in comparison to other results related to ZnO powder and ZnO/Zeolite composites, the additional diffraction peaks of 35.65° and 35.89 and 31.68 and 31.29° for Ze-ZnO nanorods and Ze-ZnO nanoflakes respectively as represented on Fig. 8 (b) and (c). These peaks are assigned to the (002) peak of

ZnO particles with hexagonal wurtzite structure (Sacco et al., 2018; Li et al., 2018). The presence of (002) peak further indicates the high preferred orientation growth of ZnO.

4.1.5 EDS analysis

After investigation of morphology, it should be specified which elements are there in the synthetic products. So, the EDAX was used for the determination of elements. Fig. 9 (a), (b), (c) and (d) shows the EDAX images of zeolites, Ze-ZnO nanorods, Ze-ZnO nanoflakes respectively. Fig. 9 (a) specifies that Na, O, Al, Si are present in the structure of zeolites with some traces of C which implies that there was incomplete conversion of CFA to the zeolite structure. The elemental composition of Ze-ZnO nanorods and Ze-ZnO nanoflakes was almost the same consisting of O, Zn, Al, Si, K, Ti, Fe, and C {Figs. 9 (b) and (c) respectively}. The presence of Fe, Ti could be due to the grade of zinc nitrate used which was of 98% purity. The zeolites seeded with ZnO consisted of O, Na, Al, Si and C and is presented in figure 9 (d).

4.1.6 TGA analysis

Figure 10 shows the TGA curves for the zeolitic materials and CFA which gives an approximation weight loss of the samples with temperature, to evaluate the thermal stability of the samples. The curves labelled (a), (b), (c), (d) and (e) represent Ze-ZnO nanorods, zeolites, CFA, Ze-ZnO nanoflakes and ZnO seeded zeolites respectively. The ZnO seeded zeolite showed the highest weight loss (17%), followed by zeolites (13%), then Ze-ZnO nanorods (7%) and Ze-ZnO nanoflakes (6%). The CFA had the least weight loss of (4%). This weight loss is attributed to loss of zeolitic water (Reyes et al., 2010).

4.2 Cation uptake capacity of Ze-ZnO nanorods and Ze-ZnO nanoflakes

Table 4 compare the measured uptake capacity of Pb^{2+} and Cd^{2+} using Ze-ZnO nanorods and Ze-ZnO nanoflakes after 1 hr of adsorption. The initial concentration in both cases was 300 ppm. The Ze-ZnO nanoflakes proved to be the most effective in removing Pb^{2+} in aqueous solution with an adsorption capacity of 74.00 mg/g against 62.50 mg/g which was obtained for Ze-ZnO nanorods. Both products proved to be effective in the uptake of Pb^{2+} . The adsorption capacity agreed for Ze-ZnO nanoflakes was in good agreement with the 74.66 mg/g reported by (Ruchi et al., 2016). The adsorption capacities for Cd^{2+} were 15.55 mg/g and 11.31 mg/g

for Ze-ZnO nanorods and Ze-ZnO nanoflakes respectively. These adsorption capacities are in line with the tentative order for affinity of different ions in zeolite exchange sites reported by (Moreno et al., 2001): $Fe^{3+} > Al^{3+} \ge Cu^{2+} \ge Pb^{2+} \ge Cd^{2+} > Tl^+ > Zn^{2+} > Mn^{2+} > Ca^{2+} = Sr^{2+} > Mg^{2+}$. In this case the zeolitic material had higher affinity for Pb^{2+} than Cd^{2+} .

The Langmuir adsorption isotherm was used to analyse the equilibrium data according to the equation in a similar way as reported elsewhere (Ruchi et al., 2016; Maity and Ray, 2018). The Langmuir equation is represented as:

$$C_e/q_e = 1/q_{max}K_L + C_e/q_{max}$$
.....(16)

 C_e is the equilibrium concentration of the dye in solution, q_e is the equilibrium amount of the ion adsorbed, q_{max} is the maximum adsorption capacity and K_L is the Langmuir adsorption constant. The Langmuir adsorption isotherm is based on the monolayer adsorption formula while neglecting the lateral interactions between the adsorbed and the adsorbent. Figure 12 shows the equilibrium adsorption isotherm for Pb²⁺ and Cd²⁺ using 0.1, 0.15, 0.2, 0.25 and 3.0 g of the adsorbent at an initial concentration of 300 ppm of the heavy metals. The samples were allowed to shake for 90 minutes. It was shown than the adsorption capacity increased with increase in the adsorbent concentration for both Pb²⁺ and Cd²⁺. However, the adsorption capacity of Cd²⁺ was much lower 25.5 mg/g compared to that of Pb²⁺ 71 mg/g. The regression curve, *Cf/qe* versus *Ce* where *Cf* is the final concentration is represented in Figs. 13 and 14. It was used to obtain values of K_L (energy of reaction) and q_{max} (maximum adsorption capacity) for Pb²⁺ and Cd²⁺ respectively. The K_L values were found to be 0.124 L/mg and 251.02 L/mg. this shows that adsorption for Cd requires more energy compared to that of Pb²⁺. The R² values were found to be 0.98 and 0.92 for Pb²⁺ and Cd²⁺ respectively. The adsorption of both heavy metals on Ze-ZnO nanorods was represented well by the Langmuir model.

Figure 15 shows the effect of time and the adsorption of Pb^{2+} and Cd^{2+} on Ze-ZnO nanorods. The initial concentration of Pb^{2+} and Cd^{2+} was 300 ppm while 0.2 g of Ze-ZnO nanorods was used. The equilibrium was reached at ~30 minutes showing and adsorption capacity of 71 mg/g and 26 mg/g for Pb^{2+} and Cd^{2+} respectively. The observed adsorption capacity of Ze-ZnO nanorods was lower than that for Ze-ZnO nanoflakes 74.66 mg/g but higher than that of zeolites 45.96 mg/g (Ruchi et al., 2016). The variation in adsorption capacities is due to changes in surface characteristics. More than 94% of Pb^{2+} was adsorbed at 60 minutes whilst only 23% of Cd^{2+} was only adsorbed. The pseudo second order kinetics was applied to study the mechanism of heavy metal adsorption on Ze-ZnO nanoroda and can be represented mathematically represented as shown below (Moraes et al., 2018):

where *qe* and *qt* are adsorption capacity of the adsorbent in mg/g at equilibrium and at a time *t* respectively. *k* is the pseudo second order rate constant (gmg⁻¹min⁻¹). The linear plot of t/qt versus t is shown in figure16, which shows a linear pseudo second order kinetic pattern having R^2 value of 0.9754 and a rate constant *k* of 3.06 x 10⁻² gmg⁻¹min⁻¹. This means that the chemical process be the rate determining step in the adsorption (Nguyen et al., 2015).

4.3 Methylene Blue Dye degradation studies

To examine the photocatalystic activities of Ze-ZnO nanorods and Ze-ZnO nanoflakes, photodegradation experiments were conducted with methylene blue dye under UV irradiation for 6 hrs and measuring the remaining concentration using UV/Vis spectroscopy at 650 nm as shown in figure 17. The degradation efficiencies of methylene blue dye shown in figure 18 were calculated using Beer Lambart Law, which gives the relationship between concentration (C) and absorbance (A) of the dye at time (t) as:

Degradation efficiency =
$$\begin{bmatrix} C_0 - C \\ C_0 \end{bmatrix} * 100\% = \begin{bmatrix} A_0 - A \\ A_0 \end{bmatrix} * 100\% \dots \dots \dots \dots \dots (18)$$

where C_0 and A_0 are the initial concentration and absorbance of the dye at initial time t_0 . The degradation efficiencies of Ze-ZnO nanorods and Ze-ZnO nanoflakes were almost the same, 95.61% and 96.87% respectively but generally decreased as the initial dye concentration increased from 5ppm to 75ppm for Ze-ZnO nanoflakes. Similar results have been reported for the photo-catalytic oxidation of other dyes (Ibrahim, 2017; Kannusamy and Sivalingam, 2013; Hameed, 2008; Nandi,Goswami and Purkart, 2009). Figure 19 shows photo-catalysis results of Ze-ZnO nanorods for 6hrs expose in the sun and increase in dye concentration from 5ppm to 75 ppm decreases the degradation efficiency from 97.62% to 96.25%. This can be attributed to the fact that when the concentration of the dye increases, the amount of dye adsorbed on the surface of the Ze-ZnO nanorods increases thus blocking the active sites of the catalyst affecting the photocatalytic activity of Ze-ZnO nanorods particles. Increase in the dye concentration also

reduces the path length of photon entering the dye solution. At high dye concentration, large amount of the UV light may be absorbed by the dye concentration rather than the catalyst thereby reducing catalyst efficiency. The photo-decomposition kinetics of methylene blue dye was studied using a variety of kinetic models and it was found to follow the first-order kinetics model. Equation 16 describes the linear form of the first order reaction (Ruchi et al., 2016). Figure 20 shows the photo degradation of methylene blue dye as a function of time when a solution containing Ze-ZnO nanorods and Ze-ZnO nanoflakes where exposed to solar irradiation for 6 hrs. The initial concentration of the methylene blue dye was 50 ppm and the adsorbent dosage was 200 mg. The photo degradation of Ze-ZnO nanoflakes reached equilibrium at 210 minutes and for Ze-ZnO nanorods, equilibrium was reached at 240 minutes. Figure 21 shows the correlation data showed R² values of 0.96 and 0.94 for Ze-ZnO nanorods and Ze-ZnO nanoflakes respectively which followed the pseudo first order kinetics. The rate constants obtained were $1.68 \times 10^{-2} \text{ s}^{-1}$ and $2.2 \times 10^{-2} \text{ s}^{-1}$ for Ze-ZnO nanorods and Ze-ZnO n

Where A_0 is the initial concentration of methylene blue dye at t = 0 and k is the rate constant.

Figure 22 shows that adsorption kinetics of methylene blue dye on Zn-ZnO nanorods is time dependant at an initial concentration of 75 ppm of dye and 0.2 g of the catalyst. The adsorption equilibrium is reached at 300 minutes with the adsorption capacity of 18.19 mg/g. Adsorption plays a significant role in photo degradation process as the organic molecule is first adsorbed on the catalyst surface followed by photo degradation. The low adsorption capacity can be attributed to low surface area. Another factor can be because in physisorption processes adsorption capacity increases with increase in initial dye concentration, in this experiment a low dye initial concentration of 75 ppm was used. Analysis of various models reveals adsorption of methylene blue dye by Ze-ZnO nanorods is pseudo- second order suggesting that the mechanism is physisorption process. This model was applied to study the mechanism of adsorption on Ze-ZnO nanorods and is represented by equation 16. The linear plot of t/qt versus t is shown in figure 23, which shows a linear pseudo second order kinetic pattern having \mathbb{R}^2 value of 0.9782 and a rate constant k of 3.56×10^{-2} gmg ⁻¹min⁻¹. Adsorption isotherms are used to indicate the interaction at the solid liquid interfaces. The Langmuir adsorption isotherm

represented mathematically as shown in equation 16 (Ruchi et al., 2016). Figure 24 shows the equilibrium adsorption isotherm for the adsorption of methylene blue dye on Ze-ZnO nanorods. Figure 25 shows the linear regression plot of $C_{f'}q_e$ versus *Ce*. The adsorption capacity was found to be 18.19 mg/g and energy of the reaction K_L was found to be 4,0916 L/mg. The methylene blue molecule [C₁₆H₁₈N₃SCl] would dissociate into [C₁₆H₁₈N₃S⁺] and Cl⁻ ions in aqueous medium and the positive ion is expected to have a higher affinity for the zeolitic surface. Thus the dye molecules are expected to rapidly migrate from the solution to the interphase of the photocatalytic core shell material.

5.1 Conclusions

According to the characterisation results zeolites were successfully synthesised using hydrothermal method. The Ze-ZnO nanoflakes and Ze-ZnO nanorods were successfully synthesised using a combination of hydrothermal and one pot homogeneous precipitation method. Both Ze-ZnO nanoflakes and Ze-ZnO nanorods showed enhanced adsorption capability in the removal of Pb, Cd and methelylene blue dye. However, the adsorption capacities of the Ze-ZnO nanorods were lower compared to those of Ze-ZnO nanoflakes. This is due to the large surface area of the Ze-ZnO nanoflakes. The adsorption of heavy metals and degradation of MB dye on followed pseudo second order kinetics for Ze-ZnO nanorods. The photocatalytic activity of Ze-ZnO nanoflakes and Ze-ZnO nanorods on the degradation of methylene blue dye fitted in the first order kinetic plot. The adsorption isotherms of Pb, Cd and methylene blue dye fitted perfectly into the Langmuir isotherm indicating monolayer adsorption on the Ze-ZnO nanorods. The multifunctional characteristics of Ze-ZnO nanorods were established involving adsorption and photo degradation therefore it can qualify as an alternative to existing water treatment methodologies.

5.2 Recommendations

I recommend the optimisation of the method used for synthesising zeolites. This can be done using increased synthesis temperature, varying sodium hydroxide concentration and washing the zeolite to a lower pH value so that zeolites with largest surface area can be obtained. I also recommend complete analysis so that the optimum water purification capacity of the Ze-ZnO nanorods, for example, studying the effect of temperature, the effect of pH, the effect of ionic strength. Since ZnO is known to possess antibacterial properties, I also recommend testing the antibacterial properties of Ze-ZnO nanorodes. Testing if the material can be used again would also be important in determining the cost- effectiveness of the Ze-ZnO nanorodes.

Aldahri, T.; Behin, J.; Kazemian, H.; Rohani, S. Fuel. 2016, 182, 494-501.

- Alshameri, A.; Ibrahim, A.; Assabri, A.M.; Lei, X.; Wang, H.; Yan, C. *Powder Technol.* **2014**, 258, 20-31.
- Alessandro, D.M.; Maria, E.F.; Vittorio, P.; Giuliana, I. *Mater. Sci. Semicond. Process.* **2017**, 69, 44-51
- Alvarez, A.E.; Garcia, S.A.; Querol, X. Water Res. 2003, 37, 4855-4862
- Batistela, V.R.; Fogoca, L.Z.; Favano, S.L.; Caetano, W.; Fernandes-Machado, N.R.C.; Hioka, N. *Colloids and Surf.*, A. **2017**, 513, 20-27
- Catalfamo, P.; Corigliano, F.; Patrizia, P.; Di Pasquale, S. J. Chem. Soc. 1993. 89, 171–175.
- Chigondo, M.; Guyo, U.; Shumba, M.; Chigondo, F.; Nyamunda, B.; Moyo, M.; Nharingo; T. *Eng. Sci. Technol.* **2013**, 4, 714-721.
- Fenoll, J.; Ruiz, E.; Hellin, P.; Flores, P.; Navarro, S. Chemosphere. 2011, 85, 1262-1268
- Georgiev, D.; Bogdanov, B.; Angelova, K.; Markovskal, I.; Hristov, Y. *International Science Conference*. **2009**, pp 1-5
- Hameed, B. J. Hazard. Mater. 2008,154, 204-212.
- Henandes-Carrillo, M. A.; Torres-Ricardez, R.; Garcia-Mendoza, M. F.; Ramirez-Morales, E.;
- Rojas-Blanco, L.; Diaz- Flores L.L.; Supulveda-Palacios, G.E.; Paraguay-Delgado, F.; Perez-Hernandez, G. *Catal. Today.* 2018, (article in process).
- Hildebrando, E. A.; Andrade, C. G. B.; Junior, C. A. F. R.; Angelica, R. S.; Diaz, F. R. V.; Neves, R. F. *Mater Res.* **2014**, 1, 1-6
- Hollman, G. G.; Steenbruggen, G.; Janssen-Jurkovicova, M. Fuel. 1999, 78, 1225–1230.
- Ismail, A. S; Mamat, M.; Malek, M. F.; Abdullar, M. A. R., Sin, M. D.; Rusop, M. Amer. Inst. Phys, 2016. 1733, 1-6
- Izidoro, J. C.; Fungaro, D. A.; Abbott, J. E.; Wang, S. Fuel. 2013, 103, 827-834
- Juan, R.; Herna'ndez, S.; Querol, X.; Andre's, J. M.; Moreno, N. PROGRES Workshop on Novel Products from combustion residues, Morella, Spain, 2001. 219–222.
- Kannusamy, P.; Sivalingam, T. Colloids Surf., A. 2013, 108, 229–238.
- Lin, C. F.; Lo, S. S.; Lin, H. Y.; Lee, Y. J. Hazard Mater. 1998, 60, 217-226.
- Li, Y.; Li, L; Yu, J. Chem. 2017, 3, 926-949
- Liang, S.; Xiao, K.; Mo, Y.; Huang, X. J. Membr Sci. 2012, 394, 184-192

- Li, Z.; Wang, L.; Meng, J.; Liu, X.; Xu, J.; Wang, F.; Brooke, P. J. Hazard Mater. 2018, 344, 1-11
- Loiola, A. R.; Andrade, J. C. R. A.; Sasaki, J. M.; Silva, L. R. D. J. Colloid Inter Sci. 2012, 367, 34–39.
- Maity, J.; Ray, S. K. Carbohydr. Polym. 2018, 182, pp 159-171
- Margeta, K.; Logar, N. Z.; Siljeg, M.; Farkas, A. *Water Treatment*. 2013. http://www.intechopen.com/books/water-treatment/natural-zeolite-in-water-treatment-howeffective-is-their-use (accessed 15 April, 2018)
- Mohamed, W. S.; Abu-Dief, A. M. J. Phys. Chem. Solids. 2018, 116, 375-385
- Moraes, N. P.; Silva, F. N.; Silva, M. L. C.; Campos G.P.T.; Rodrigues L.A. *Mater. Chem. Phys.* **2018**, 214, 95-106
- Moreno, N.; Querol, X.; Ayora, C. Environ Sci. Technol. 2001, 35, 3526–3534.
- Murayama, N.; Yamamoto, H.; Shibata, H. Miner. Process. 2002, 64, 1-6
- Nandi, B.; Goswami, A.; Purkait, A. J. Hazard Mater. 2009, 161, 387-395.
- Ong C. B.; Yong, N. L.; Mohamed, A. W. *Renewable and Sustainable Energy Reviews*. 2018, 81, 536-551
- Rauf, M. A.; Ashraf, S. S. Chem. Eng. J. 2009, 151, 10-18
- Ruchi, S.; Richa, S.; Sangeeta, T.; Sandeep, K. T. Appl. Mater. Interf. 2016, 8, 12520-12527
- Park, M.; Choi, C. L.; Lim, W. T.; Kim, M. C.; Choi, J.; Heo, N. H. *Microporous Mesoporous Mater.* **2000**, 37, 81–89.
- Patane, G.; Di Pascuale, S.; Corigliano, F. Ann Chim. 1996, 86, 87–98.
- Sacco, O.; Vaiano, V.; Matarangolo M. Sep. Purif. Technol. 2018, 193, 303-310
- Salem, I. A.; Salem, M. A.; El-Ghobashy, M. A. J. Mol. Liq. 2017, 248, 527-538
- Shikha, D.; Sushmita, B.; Siddh, N. U.; Yogesh, C. S. J. Mol. Liq. 2017, 240, 656-677
- Tunde, V.O.; Pieter, V. D; Leslie, F. P. Utrason Sonochem. 2016, 31, 342-349
- Shoumkova, A.; Valeria, S.; (2012).
- Suyama, Y.; Katayama, K.; Meguro, M. Utrason. Sonochem. 1996, 2, 136-140
- Stanley, E. M. Environ. Sci. Technol. 2001, 1, 394
- Querol, X.; Plana, F.; Alastuey, A.; Lo´pez-Soler, A. Fuel. 1997, 76, 793-799.
- Querol, X.; Plana, F.; Uman^a, J.; Alastuey, A.; Andre's, J. M.; Juan, R.; Lo'pez-Soler, A. *Int. J. Coal Geol.* **1999**, 176.
- Querol, X.; Moreno, N.; Umana, J. C.; Alastuey, A.; Hernandez, E.; Lopez-Soler, A.; Plana, F. *Int. J. Coal Geol.* **2002**, 50, 413-423.

Wang, J. Q.; Huang, Y. X.; Pan, Y.; Mi, J. X. *Microporous Mesoporous Mater*. **2014**, 199, 50-56

Wang, C.F.; Li J. S.; Wang, L. J.; Sun, X. Y. J. Hazard Mater. 2008, 155, 58-64.

Zhang, F.; Chen, X.; Wu, F.; Ji, Y. Colloid Surf., A. 509,474-483

Zheng, Y.; Zhu, Y.F.; Wang, A. Q. Chem Eng.J. 2014, 257, 66-73.