

**BINDURA UNIVERSITY OF SCIENCE EDUCATION  
FACULTY OF SCIENCE AND ENGINEERING  
DEPARTMENT OF CHEMISTRY**



**REMOVAL OF CAFFEINE FROM WATER USING CLAY-BIOCHAR SUPPORTED  
ZERO VALENT IRON NANOCOMPOSITE**

**BY**

**EMMANUEL ANESU MUTANDIRO**

**(B1747974)**

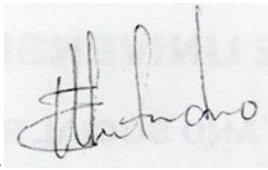
**Dr W Munzeiwa (Supervisor)**

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DEGREE IN CHEMICAL TECHNOLOGY**

**AUGUST 2020**

**Declaration**

I, Emmanuel Mutandiro, hereby declare that this research project is my original work.



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## Approval Form

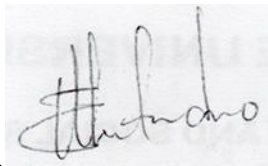
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### **REMOVAL OF CAFFEINE FROM WATER USING CLAY-BIOCHAR SUPPORTED ZERO VALENT IRON NANOCOMPOSITE**

Submitted by Emmanuel Mutandiro

In partial fulfilment of the requirements for the *BACHELOR OF SCIENCE HONOURS*

*DEGREE IN CHEMICAL TECHNOLOGY*



..... 19..../...02./2023

*(Signature of Student) Date*

*(Signature of Supervisor) Date*



..... 19/....02.../...2023

*(Signature of the Chairperson) Date*

## **Dedication**

To everyone who made this a success

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First and foremost, I would like to thank the dear Lord God for the opportunity to lead a happy life and the opportunity to pursue my studies in good health. I would like to extend my deepest gratitude to Dr W Munzeiwa for his guidance, knowledge and the constant supervision. The study would not have been a success without his tireless efforts. In a special way I want to thank Dr N Muchanyereyi for the help she gave me during my studies. I would also like to thank the Chemistry Department as a whole for investing their precious time in helping me in my research study. Their contributions were of paramount importance. Lastly, I would like to give my thanks to my family and friends for their undying love, support and encouragement that kept me optimistic even in the darkest of times. God bless.

## **Abstract**

In this study, Clay-Biochar supported nano zerovalent iron composite was synthesized following reduction of iron by sodium borohydride. The composite was characterized by FT-IR spectroscopy. The removal of Caffeine by C-B-nZVI was examined under various experimental conditions. The composite showed up to 98% removal at pH 7, 30 minutes contact time, 1 g adsorbent dosage, 2 mg/L initial Caffeine concentration and all temperatures. The adsorption equilibrium was fitted to Langmuir and Freundlich adsorption isotherms. Adsorption favoured Langmuir isotherm to a great extent with a correlation factor ( $R^2$ ) of 0.992 for Langmuir and 0.6789 for Freundlich. The reaction kinetics was pseudo-second order. The results showed high efficiency of clay, and biochar as support materials for nano zerovalent iron. The C-B-nZVI composite has great potential for use as an adsorbent to remediate water from emerging organic micropollutants such as caffeine.

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## **Chapter 1: Introduction**

### ***1.1 Background***

Pharmaceuticals and personal care products (PPCP) can be considered a milestone in scientific advancement. Their advent has ushered in an increased life expectancy and the curing of various deadly diseases (Patel et al., 2019). However because of their occurrence in the natural aquatic environment they are now recognized as emerging environmental contaminants due to the potential adverse effects these compounds pose to aquatic life and humans (Jagoda, 2015). There is currently limited information about the effects of emerging contaminants on flora and fauna and even less about their potential long-term effect at environmental concentrations on humans (Sotelo et al., 2014).

Caffeine (1,3,7- Trimethyl-3,7-dihydro-1H-purin-2,6-dion) is a bitter, white crystalline purine, a methylxanthine alkaloid with chemical formula  $C_8H_{10}O_2$ . Caffeine is considered the most widely consumed drug in the world; it acts as psychostimulant and analeptic. Its consumption occurs in beverages condiments, colanuts, analgesics, anti-congestants and diet. Caffeine is considered a chemical marker for surface water pollution due to its regular consumption, and the quantities discharged are sufficient to permit the analytical detection (Sotelo et al, 2013). In past years, most commonly applied absorbance for caffeine remediation, are activated carbon adsorption, natural clays, biochar, hydrogels beads, chitosan and its derivatives, graphene nanoplatelets (GNPs), multi-walled carbon nanotubes (MWCTNTs) (Anastopoulos et al., 2020).

Clay minerals are inexpensive, widely available, can be easily modified and provide a cost-effective alternative support material (El-maghrabi et al, 2016) and biochar an organic porous high-carbon, fine-grained, and stable material that is also a promising supporting material for nano zero valent iron (nZVI) due to its high stability and large specific surface area (Wang et al., 2019). Compared with other adsorbents, biochar and clay are more suitable platforms or matrix for synthetic composites because they are more environmentally friendly (preparation consumes low energy) and also have abundant surface oxygen-containing functional groups (Li et al., 2017).

An approach based on Zero-valent iron (ZVI) as an adsorbent in the remediation of groundwater has recently attracted a considerably wide attention (Quan et al. 2014). Zero-valent iron has been used successfully to remediate groundwater by construction of a permeable reactive barrier (PRB) of zero-valent iron. A PRB, in its simplest form, is a trench of suitable

reactive or adsorptive medium built across the flow path of a groundwater plume (Cook, 2009). Research has however shifted to the nanoscale material, because ZVI is easily passivated and has a relatively slow reaction rate due to its large size (H. Li et al., 2017). Instead of ZVI, nanoscale zero valent iron (nZVI) that is iron with a size below 100 nm, has great application potential in the field of environmental remediation because of its small particle size, high surface activity, strong reduction ability, low dosage, low cost, lower environmental risk of nZVI and massive surface adsorption sites (Zhao et al., 2017)(Wang et al., 2017)

nZVI combined with clay and biochar together could perform better for the remediation of caffeine from aqueous solution and soils because clays and biochar have a porous structure giving a large surface area and uniform pore sizes, which are of great importance for a good adsorbent, they can be used as the potential support for the fabrication of an efficient adsorbent (El-maghrabi et al, 2016)(Wang et al., 2017).

### ***1.2 Aim of study***

This study aims at synthesising a clay-biochar supported zero valent iron (C-B-nZVI), characterise it and test its capability and efficiency for the caffeine removal from water.

### ***1.3 Objectives of the study***

The objectives of the study were as follows:

- Developing a new material (to improve the higher surface area and adsorption capacity) through supporting nZVI with clay and biochar to combine advantages of clay and biochar (low cost, porosity, functional groups and natural material) and nZVI (high surface area and high adsorption/oxidation capacity)
- To characterize C-B-nZVI composites on FT-IR
- To evaluate caffeine adsorption performance of C-B-nZVI composites in different experimental conditions

### ***1.4 Statement of the problem***

Caffeine is an emerging environmental contaminant. In large doses, it can cause depletion of nerve cells and when consumed in very large doses it causes death. Caffeine is often found in surface waters and must be removed from aqueous media through different water treatment technologies (Anastopoulos et al., 2020).

In order to remove these emerging contaminants from wastewaters, varied physicochemical techniques such as ozonation, membrane technologies, and adsorption on synthetic or natural adsorbents have been proposed (Sotelo et al., 2013).

### ***1.5 Significance of study***

- ✓ Clay and biochar are cheaper options of support materials which are readily available raw materials.
- ✓ Removal of caffeine from water reduces mortality of aqua life

### ***1.6 Scope of the study***

The study will encompass the synthesis of C-B-nZVI composites, their characterisation followed by evaluation of the capability of the composites to remove caffeine from water including the thermodynamic and kinetic properties.

### ***1.7 Research questions***

1. How effective is the clay-biochar supported zero valent iron nanocomposite on the removal of caffeine from water?
2. What are the merits the adsorption technique over other water remediation techniques of caffeine?

## **CHAPTER 2: LITERATURE REVIEW**

### ***2.1 Introduction***

The major focus of this chapter is the exploration of the theory that is required as well as the related work required to put this study together. The chapter also aims at presenting the work that has been previously done by other researchers, their arguments and effective contributions in the field of adsorbents and effectiveness of removal of organic compounds in water using a composite of clay, biochar and nano zero valent iron.

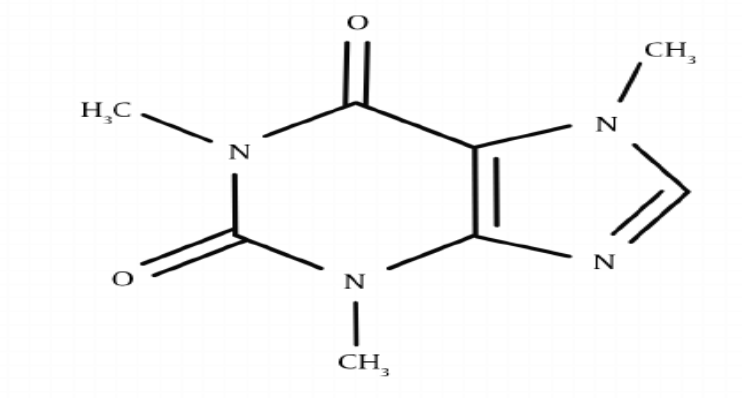
### ***2.2 Nano-zerovalent Iron***

In recent years, nZVI has been successfully used for the treatment of many contaminants from wastewater and contaminated soil, including inorganic pollutants(Wang et al., 2019). The use of nanoscale zero-valent iron (nZVI) instead of using micro/macro-scale  $\text{Fe}^0$  (zerovalent iron) materials could potentially eliminate the need for using PRBs and be more effective in both cost feasibility and contaminant remediation(Cook, 2009). However, the intrinsic properties of nZVI, such as large surface area, high surface energy, and reactivity with the surrounding media, would cause severe aggregation of iron nanoparticles during preparation and storage as well as agglomeration to form larger micrometre particles with a significant drop in reactivity and mobility which restricts its field of application (Han et al., 2015). Its easy oxidation to iron oxide in aerobic environment, make the application of nZVI limited to anaerobic medium (Harman et al., 2016). When the surface of the nZVI is coated with the oxidized precipitate nZVI, the activity of the nZVI is substantially undermined causing a decrease in the speed and the effect of the reaction. The transport of nZVI particles is also usually very difficult when added into soil. In order to conquer nZVI aggregation and enhance the reactivity, many porous carbon materials such as graphene nanosheets/nanotubes and activated carbon have been commonly applied as supporters, owing to their high surface area and specific pore structure that could inhibit oxidation and aggregation (Wang et al., 2017).

### ***2.3 Caffeine***

Caffeine (1,3,7-Trimethyl-3,7-dihydro-1H-purin-2,6-dion) is an alkaloid belonging to methylxanthine family with the chemical formula( $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$ ). Caffeine is a major drug used in the world, consumed by approximately ninety percent of the world population (Rosal et al., 2009). In humans, caffeine acts as a central nervous system (CNS) stimulant, temporarily warding off drowsiness and restoring alertness. Therefore, there is an important occurrence of this pollutant not only into some industrial effluents but also into domestic wastewaters

(Indermuhle et al., 2013). Caffeine acts as psychostimulant and analeptic and many drugs contain caffeine (for example analgesics, antihistamines, diet pills, cold remedies, and stimulants of psychophysical activity) (Anastopoulos et al., 2020). It is important to highlight that human body has no nutritional need for caffeine, and could survive without it. Although the most important caffeine source is from natural plants, it can also be artificially synthesized and added to certain foods and can be used for improving mental alertness and also as a cream for redness of skin (Zarzar et al., 2015).



**Figure 2:1-** Structure of caffeine

#### **2.4 Environmental and Health Concern of caffeine**

Due to huge consumption of caffeinated food, beverages and medicines around the world, caffeine has been considered as the most representative pharmaceutically active compound (PhACs) pollutant based on its higher abundance in environment and its indicator property for anthropogenic inputs of PhACs to water bodies (Li et al., 2020). Caffeine affects our brain function which causes change in our behavior, mood cognition and consciousness (Erukainure et al., 2017). About three percent of our intake of caffeine is passed through our urine unchanged which means it ends up in water ways or when products such as beverages of pharmaceuticals are disposed of through household plumbing and sewer systems (Knee et al., 2010). Importantly definitive evidence has been provided that environmentally relevant caffeine concentrations exert adverse impacts on aquatic species and terrestrial insects, which included lethality, decreasing general stress including oxidative stress and lipid pre oxidation affecting energy reserves and metabolic activity, neurotoxic effects, affecting reproduction and development (Li et al., 2020). The effects of caffeine in aquatic life is similar to that on humans



it increases heart rate and activity (Capolupo et al., 2016). A study by (Rodriguez et al., 2011) on intertidal mussel showed that even low levels of caffeine caused native mussel to respond by releasing an amount of stress hormones. Another study by (Knee et al., 2010) linked caffeine concentrations in ground and surface waters to wastewater contamination and suggested that caffeine could be considered a wastewater tracer.

## ***2.5 Other water treatment methods***

Many treatment technologies are introduced to remove caffeine from wastewater, including activated carbon adsorption, biodegradation, ozonation, electrochemical oxidation but these processes have a number of limitations such as low efficiency, incomplete degradation, and high energy consumption which limit the wide application of these technologies (Wang et al., 2017).

### *2.5.1 Activated carbon adsorption*

The high measure of surface area of the activated carbon, its microporous character and surface chemical nature make it highly efficient as a potential adsorbent (Sarici-özdemir et al., 2018). Traditional systems that aim at the removal of organic contaminants from water, including some pharmaceuticals, still revolve around the use of activated carbons but it is known that their capacity and selectivity greatly decrease due to competition from the many species involved in the water matrix (Cabrera-lafaurie et al., 2012)

### *2.5.2 Ozonation*

Ozonation refers to a process whereby ozone is applied to waste water in order to remove contaminants from water. Decomposition of organic solutes with ozone follows two paths which are direct oxidation through the attack of ozone at the electron rich site of the solute and indirect oxidation that ozone produces hydroxyl radicals after radiolysis or photolysis. These radicals exhibit little solute selectivity and react very rapidly with organic and inorganic solutes (Torun et al., 2014). Specifically, the degradation by ozonation is slow and many reaction intermediates and transformation products are found (Indermuhle et al., 2013).

### *2.5.3 Electrochemical oxidation*

Electrochemical oxidation can be obtained by both direct and indirect processes and the effectiveness of this process strongly depends on the treatment conditions and on the nature of the electrode materials (Periyasamy et al., 2018). The oxidation of water is principally based on the hydroxy radical generated on the surface of the electrode. The radicals generated in situ

are expected to react with persistent organic pollutant irrespective of its nature (Periyasamy et al., 2018). The main drawback is the low efficiency, usually explained by a mass transfer control of the oxidation rate. Coupling ultrasounds (US) with CDEO into a sonoelectrolytic process (Conductive-Diamond Sonoelectrochemical Oxidation, CDSEO) is expected to produce a great improvement in the results (Indermuhle et al., 2013).

## ***2.6 Water purification using adsorption***

Adsorption is the most widely used process due to its removal efficiency, low energy demand, less chemical investment, simplicity of operation and low implementation costs when compared with other treatment methods (Harman et al., 2016). Adsorption is a surface accumulation of adsorbate on adsorbent. It occurs when a solution containing absorbable solute comes into contact with a solid with a highly porous surface structure causing some of the solute molecules from the solution to be concentrated or deposited at the solid phase by liquid-solid intermolecular forces of attraction (Rashed, 2013). The adsorbate is the solute retained on the solid surface while the solid on which it is retained is called the adsorbent. In the adsorbent, all the bonding of the constituent atoms of the material are filled by other atoms of the material (Zhang, 2019). However, atoms on the surface of the adsorbent are not wholly surrounded by other adsorbent atoms and therefore can attract adsorbates. The adsorption process is generally classified as physisorption (characteristic of weak Van Der Waals forces) or chemisorption (characteristic of covalent bonding). It may also occur due to electrostatic attraction.

### ***2.6.1 Adsorption by clay-biochar composite***

Montmorillonite as one of the most common clay minerals has great potential in removal of heavy metals and organic compounds due to special physical and chemical properties. Montmorillonite was composed of one octahedral unit inner layer between two tetrahedral outer layers. The layers were negatively charged and balanced with hydrated cations existing in the interlayer spaces. However, montmorillonite tended to expand easily, which limited the actual application in wastewater treatment directly. Therefore, the modification of montmorillonite by adding biochar was economic and feasible method to increased adsorption capacity (Wang et al., 2019).

### *2.6.2 Adsorption by Clay-nZVI*

Owing to an extremely small size and large surface area, the iron nanoparticles proved to be highly reactive as compared to granular iron, which is usually applied in reactive barriers and for in situ water treatment. It can also remove a substantial amount of organic pollutants, inorganic anions, and dissolved heavy metals from the solution in a highly efficient manner (Patanjali et al., 2019). However, the ultra-fine powder on nZVI have a tendency to agglomerate into larger particles which reduces their ability to perform their role on both the effective surface area and catalytic properties. Using supporting material for nZVI is a promising way to solve these problems. Clay minerals as abundant natural resources are appropriate candidates to act as supporting materials; their adsorption capacity attracts contaminants to the surface and thus enhance the efficiency of nZVI particles (Ezzatahmedi et al., 2017). Clay-nZVI mixing is a relatively new technology for in situ source zone remediation. The technology significantly changes the hydraulic and chemical properties of the source through soil mixing with the addition of zero valent iron (ZVI) and clay (Fjordbøge et al., 2012). Remediation by clay-nZVI composites is mainly attributed to the synergetic effect between adsorption by the clay mineral and removal by nZVI particles that is why the composite materials have higher removal efficiency compared to nZVI particles and neat clay minerals (Ezzatahmedi et al., 2017).

### *2.6.3 Adsorption by biochar-nZVI*

Biochar can be used to modify nZVI to optimize the dispersion and/or stabilization of nZVI for water treatment (Han et al., 2015). Biochar has a porous structure and a large specific surface area and also possesses large numbers of oxygen-containing functional groups that are formed during the pyrolysis process. These characteristics suggest biochar may be used as an alternative to activated carbon to remove organic contaminants and heavy metals from fluids (Li et al., 2017). Due to the porous structure of biochar it has demonstrated to have excellent abilities to remove a range of contaminants from aqueous solutions. Biochar can be derived from a variety of biomass such as wood, leaves, manure and agricultural wastes through the pyrolysis under oxygen limited conditions. In addition, it does not need a treatment for further activation like active carbon. Therefore, biochar may be a more cost-effective and readily accessible alternative material for engineering application as a template of nZVI (Han et al., 2015).

## **2.7 Material characterization**

### **2.7.1 FT-IR Spectroscopy**

FT-IR is used in the determination of the structural information of a given compound species, the technique is used to measure the intensity of infra-red radiation with respect to wavelength or frequency (Jagoda, 2015). The technique can analyze liquids, gases or solids, the technique is used to determine the different functional groups in samples. Both organic and inorganic compounds and ions absorb infra-red radiation within the region of 400-4000  $\text{cm}^{-1}$  hence that is the region that is usually used for analysis (Anis et al., 2018).

### **2.7.2 X-ray diffraction**

The analytical technique is used in almost every field from medical sciences to engineering sciences, characterization of materials using X-rays dates back into time. X-ray diffraction is used for analysis of solid materials be it amorphous or crystalline, primarily in determination of important features of a certain material like its crystallite size, x-ray patterns and crystal structure. The full width at half maximum (FWHM) of a diffraction peak is the most common technique used to estimate the average size of the crystallite, the method uses the equation below

$$(2.1)$$

Where:  $d$  is the crystallite size,  $K$  is a constant and is close to unity,  $B$  is corrected FWHM diffraction angle and  $\lambda$  is the diffraction wavelength.

## **2.8 Adsorption Studies**

An adsorption isotherm is the presentation of the amount of solute adsorbed per unit weight of adsorbent as a function of the equilibrium concentration in the bulk solution at constant temperature (Rashed, 2013).

### **2.8.1 Langmuir Adsorption Isotherm**

The Langmuir isotherm assumes monolayer adsorption on a uniform surface with a finite number of adsorption sites. Once a site is filled, no further sorption can take place there. The isotherm equation is derived theoretically based on assumptions that there is equilibrium between the residual molecules in solution and those on the surface of the adsorbent, the isotherm assumes that a site on the surface of the adsorbent can only adsorb one atom and a monolayer is formed (Li et al., 2019). The equation for the isotherm can be written as illustrated below:

(2.2)

Where:  $q_e$  is the equilibrium content in the adsorbent ( $\text{mg/g}^{-1}$ ),  $q_m$  is the maximum adsorption capacity ( $\text{mg g}^{-1}$ ),  $K_L$  is the constant for the Langmuir model ( $\text{L mg}^{-1}$ ) and  $C_e$  is the equilibrium concentration of adsorbate in the solution ( $\text{mg L}^{-1}$ ).

The non-linear Langmuir isotherm expression can be converted into the following linear model

(2.3)

### 2.8.2 *Freundlich Adsorption Isotherm*

The isotherm assumes that an adsorbent does have a heterogeneous surface and that each and every molecule possesses differing potential of adsorption. The isotherm equation also shows both irreversible and reversible adsorption processes, a monolayer adsorption also is not forbidden. Below is the isotherm's adsorption equation (Rashed, 2013).

(2.4)

The equation can be rearranged to give a linear form of the equation as shown below

(2.5)

Where:  $K_f$  represents the Freundlich adsorption isotherm constant ( $\text{mg/g}$ ),  $Q_e$  is the adsorption capacity ( $\text{mg/g}$ ),  $C_e$  represents the residual adsorbent concentration in ( $\text{mg/L}$ ) and  $n$  is the adsorption intensity.

### 2.9 *Kinetic Adsorption studies*

Kinetic adsorption studies are used to describe the rate of adsorption of solutes which determines the residence period of adsorbate adsorption at the solid-solution interface which also includes processes of diffusion (Iryani et al., 2017). The mechanism is dependent on adsorbent's chemical and physical properties and also the process of mass transfer, the Pseudo first and second order kinetic reaction equations are used to analyse kinetic adsorptions (Iryani et al., 2017).

#### 2.9.1 *First Order Pseudo Kinetic Equation*

The kinetic equation explores the process of adsorption in a solid-liquid interface basing on solids capacity (Tan et al., 2008), the general form of the equation is described below:

$$(2.6)$$

Where:  $q_{eq}$  represents the adsorbed adsorbent ions at equilibrium in mg/g,  $q_t$  is the adsorbed adsorbent at time  $t$  in mg/g and  $K_{ad}$  is the pseudo first order constant

The equation can be converted into a linear form given below

$$(2.7)$$

### *2.9.2 Second Order Pseudo Kinetic Equation*

The kinetic equation illustrates how the rate of adsorption solely depends on the relative adsorption capacity of the used adsorbent and not the concentration of the adsorbate (Saleh, 2015). The kinetic equation allows determination of initial adsorption rate and the rate constant, as well as the effective adsorption capacity, the equation is given below

$$(2.8)$$

Where:  $k$  represents the pseudo second order adsorption speed constant in g/mg.min, integrating the equation gives us the equation below

$$(2.9)$$

The model with the highest correlation value ( $R^2$ ) is best fitted by the experimental data (Saleh, 2015).

### *2.10 Adsorption thermodynamics*

A number of thermodynamic parameters such as the  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  are used to study the thermodynamic characteristics of the adsorbate (Iryani et al., 2017), the Gibbs free energy can be calculated using the equation below

$$(2.10)$$

Where:  $R$  is the gas constant,  $T$  is the temperature and  $K_d$  is the distribution coefficient

To calculate  $K_d$  the equation below is used

(2.11)

Where  $C_{Ae}$  is the adsorbate amount per unit of the mass of the adsorbent and  $C_e$  is the adsorbate concentration in the solution.

To calculate  $\Delta H^\circ$  and  $\Delta S^\circ$  for the adsorption process the slope and the intercept of the Vant's equation are used as shown below

(2.12)

A negative value for the  $\Delta G^\circ$  resembles a spontaneous adsorption process, a negative value for  $\Delta H^\circ$  resembles an exothermic adsorption process whilst a negative  $\Delta S^\circ$  means the degree of freedom of the particles of the adsorbate found in the solid-liquid interface during the process of adsorption is very low (Iryani et al., 2017).

## CHAPTER 3: METHODOLOGY

### 3.1 Materials

All chemicals used; NaBH<sub>4</sub>, FeCl<sub>3</sub> and ethanol were purchased from Sigma Aldrich and used without further purification. Biochar was obtained from macadamia nuts. Clay sample was collected from a local ceramist. All solutions were prepared with deionized water.

### 3.2 Equipment

An Adam analytical scale was used in measurements of both samples and reagents, all pH measurements were done using a pH meter (Model: Li-702, Pachikula-Haryana, India). Characterization of the clay-biochar ZVI nanocomposite was done by FTIR spectrophotometer (Nicolet IS5, Thermo Fisher Scientific). A laboratory platform shaker (Model SFI, Stuart Scientific, UK) was used in stirring the samples. For determination of the removal percentage of caffeine from solution by the clay-biochar ZVI nanocomposite a UV-V's spectrophotometer (Genesis 105, Thermo Fisher Scientific) was used.

### 3.3 Synthesis of nZVI-Biochar-Clay composite

The nZVI was synthesised based on the “bottom up” reduction of ferric (Fe(III)) salt with borohydride as described by Scheme 1 (Li et al., 2006):



The nZVI-Biochar-Clay composite (nZVI-B-C) was prepared using a combination of procedures by (Üzüm et al., 2009) and Wang and Zhang (2019) with modification. Iron(III) chloride was used as an iron precursor and 1 M sodium borohydride as a reducing agent. The mass ratio of nZVI to biochar was varied while the clay was kept constant (Table 3.1). Initially, 4.0 g Fe(III) was dissolved in an ethanol and water mixture. The ethanol to water ratio (v/v) was 4:1 to ensure uniform nanoparticles. Biochar and clay (0.1 g and 0.5 g, respectively) were slowly added to the solution and the mixture was stirred on a magnetic stirrer. Sodium borohydride (1M) solution was prepared by dissolving 3.05 g NaBH<sub>4</sub> in 100 mL deionized water. Particles of nZVI were deposited on clay and biochar surfaces and in pores by adding, dropwise, 100 mL of 1 M NaBH<sub>4</sub> to the iron-biochar-clay-water mixture with vigorous stirring on a magnetic stirrer. The mixture was stirred an additional 30 min. The sodium borohydride was added in a 10% excess to ensure the complete reduction of Fe(III) to Fe<sup>0</sup>. Solid products were separated from liquid phase by vacuum filtration using two sheets of blue band Whatman



filter paper. The resultant solid particles were washed with deionized water once to remove inorganic ions then with 25 mL portions of absolute ethanol thrice to remove water, and pyrolyzed in an airtight canister to prevent iron oxidation at 400, 600, 900 °C for 1, 2, 4 h. After synthesis the composites were stored in desiccator to prevent oxidation.

**Table 3.1-** Amounts of chemical used in the synthesis of C-B-ZVI composites

Sample	Fe (g)	Bio-char(g)	Clay(g)	Ethanol/Water (mL/mL)	NaBH <sub>4</sub> /Water (g/mL)
<b>C-B-ZVIA</b>	1	0.1	0.5	10/40	3.05/100
<b>C-B-ZVIB</b>	1	0.1	0.3	10/40	3.05/100
<b>C-B-ZVIC</b>	0	0.2	1	10/40	3.05/100
<b>C-B-ZVID</b>	1	0.1	0.1	10/40	3.05/100

### **3.4 Characterization of materials**

The surface functional groups of the clay-biochar-nanozerovalent iron composite were examined by Fourier transform infrared (FTIR) spectrometer (Thermo Scientific, Nicolet iS5 iD7 ATR).

### **3.5 Adsorption experiments**

Throughout this study, caffeine solutions were prepared as follows: 1 g of analytical grade caffeine was dissolved in 1000 mL of deionized water in a volumetric flask to yield 1000 mg/L caffeine stock solution. The stock solution was then used in preparation of solutions with lower concentrations of 2 mg/L, 5mg/L, 10 mg/L, 20 mg/L, 30 mg/L, 40 mg/L, and 50 mg/L by serial dilution. Unless stated otherwise, all adsorption experiments were carried out using batch studies. The caffeine solutions were transferred into clean Erlenmeyer flasks. The solutions were then kept in a safe place until use, and were diluted in proper ratios before analysis by UV/VIS.

#### **3.5.1 Effect of the ZVI amount in sample of caffeine adsorption**

Caffeine solutions of 20 mg/L were prepared in portions of 100 mL and poured into 4 labelled flasks. Then 1 g of each of the C-B-nZVI composites with differing ZVI:Clay:Biochar ratios of sample A 1:0.5:0.1, sample B 1:0.3:0.1, sample C 0:1:0.2, sample D 1:0.1:0.1 were added and allowed to shake for 30 minutes. After shaking filtration was done and the filtrates were measured on UV/V's spectrophotometer.

### *3.5.2 Effect of initial caffeine concentration*

The effect of initial caffeine concentration on the extent of uptake were investigated as follows: caffeine solutions in portions of 100 mL having concentrations of 2, 5, 10, 20, 30, 40 and 50 mg/L were prepared then, 1 g of C-B-nZVI was measured and allowed to shake for 30 minutes. After filtration the filtrates were analysed on UV/V's.

### *3.5.3 Effect of initial solution pH*

caffeine solutions of concentration 20 mg/L were prepared in portions of 100 mL and poured into 4 labelled flasks, and the pH adjusted to 2, 4, 7, and 10 using 0.1 M or 3 M HNO<sub>3</sub> or NaOH. Then 1g of C-B-nZVI were added to each of the flasks, the solutions were shaken on the shaker for 30 minutes, filtered and the filtrates collected for analysis. The filtrates as well as the control were analysed by UV/V's spectrophotometer at 272nm.

### *3.5.4 Effect of C-B-nZVI dosage on adsorption of caffeine*

A 20mg/L solution was prepared from the 1000 mg/L stock solution, 100 mL of the 20 mg/L were measured into 4 labelled volumetric flasks. The effects of changing the initial C-B-nZVI dosage in the sorption medium on removal of caffeine in terms of adsorption capacity was examined at differing amounts of C-B-nZVI of 0.1 g, 0.4 g, 0,8 g and 1 g for 30 minutes. After shaking the 4 suspensions filtration was done and the filtrates where then measured on the UV/V's spectrophotometer at 272nm.

### *3.5.5 Effect of contact time and temperature on adsorption of caffeine*

A 20 mg/L caffeine solution was prepared from the 1000 mg/L stock solution, 100 mL of the 20 mg/L solution were measured by measuring cylinder into each of the flask followed by 1 g of the solid adsorbent. The flasks were shaken using a magnetic stirrer for different time intervals of 5, 10, 15, 20, 25 and 30 minutes and different temperatures of 20, 25 and 30 °C. The solutions were filtered and the filtrates were measured on the UV/V's spectrophotometer 272nm.

## **3.6 Adsorption Studies**

### *3.6.1 Percent Removal Capacity*

The % removal capacity of Caffeine was calculated using the equation below

$$(3.1)$$

Where:  $C_f$  is the final concentration of solution in  $\text{mg L}^{-1}$ ,  $C_i$  is the initial concentration of the solution  $\text{mg L}^{-1}$

### 3.6.2 Equilibrium Amount of adsorbate Adsorbed

The equilibrium amount of adsorbate adsorbed at equilibrium,  $Q_e$  was calculated as follows

$$(3.2)$$

Where:  $Q_e$  is the amount of adsorbate adsorbed at equilibrium in  $\text{mg g}^{-1}$ ,  $C_o$  is the initial adsorbate concentration in  $\text{mg L}^{-1}$ ,  $C_e$  is the residual concentration of the adsorbate in  $\text{mg L}^{-1}$ ,  $m$  represents the mass of adsorbent used in grams and  $V$  is the volume of Caffeine solution used in L

### 3.6.3 Freundlich Adsorption Isotherm

For the Freundlich isotherm the famous In-In form given in *equation 2.5* was used

$$(3.3)$$

Where:  $q_{eqm}$  refers to the amount of adsorbate that has been adsorbed at equilibrium in  $\text{mg g}^{-1}$ ,  $C_{eqm}$  is the concentration of adsorbate at equilibrium in  $\text{mg L}^{-1}$ ,  $K_f$  is the adsorbent capacity in  $(\text{mg g}^{-1})(\text{L mg}^{-1})$  and  $n$  represents the adsorption intensity given in  $\text{g L}^{-1}$ .

### 3.6.4 Langmuir

For the Langmuir isotherm the linear version given in *equation 2.3* was used

$$(3.4)$$

Where:  $C_e$  is the equilibrium concentration of Caffeine in  $\text{mg L}^{-1}$ ,  $Q_e$  refers to the amount of Caffeine adsorbed in  $\text{mg g}^{-1}$ ,  $Q_m$  is the maximum sorption capacity of the adsorbate Caffeine in  $\text{mg g}^{-1}$  and  $b$  represents the Langmuir isotherm constant in  $\text{L mg}^{-1}$

### **3.7. Kinetic Studies**

Kinetic studies were done using the first order and second order Pseudo kinetic equations

#### **3.7.1 First order Pseudo kinetic equation**

The integrated form given in *equation 2.6* was used

#### **3.7.2 Second order Pseudo kinetic equation**

The simplified form given in *equation 2.8* was used

### **3.8 Adsorption Thermodynamics**

To calculate the Gibbs free energy the expression in *equation 2.10* was used

## Chapter 4: Results

### 4.1 Characterization of samples on FT-IR

#### 4.1.1 FT-IR spectra of clay

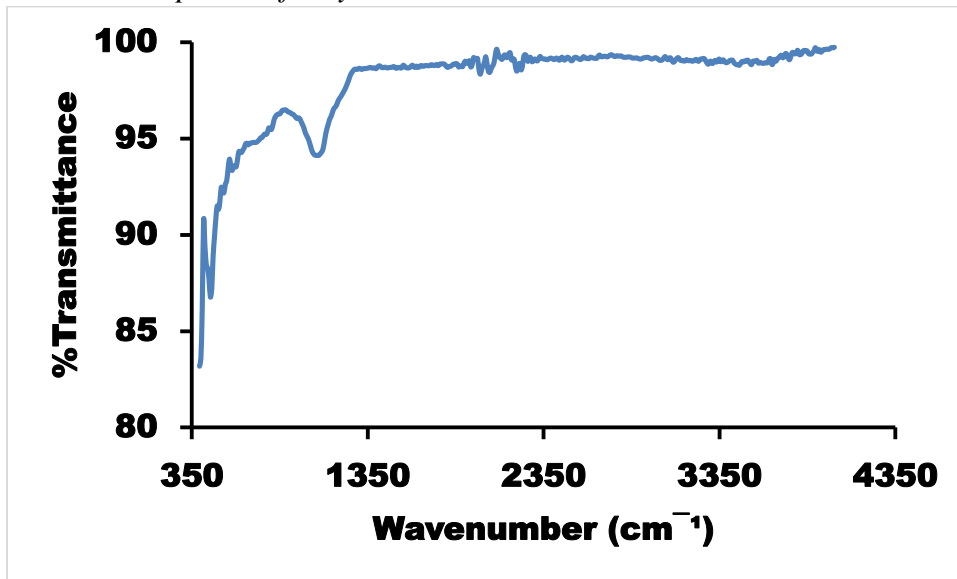


Figure 4:1 FT-IR spectrum for clay

#### 4.1.2 FT-IR of Biochar

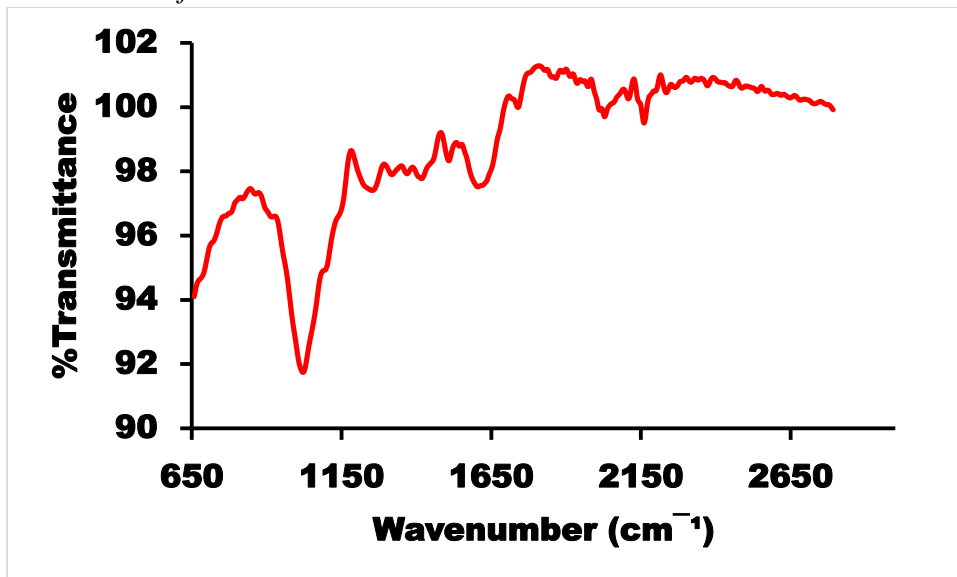


Figure 4:2 FT-IR spectrum of Biochar

#### 4.1.3 FT-IR spectra of C-B-nZVI

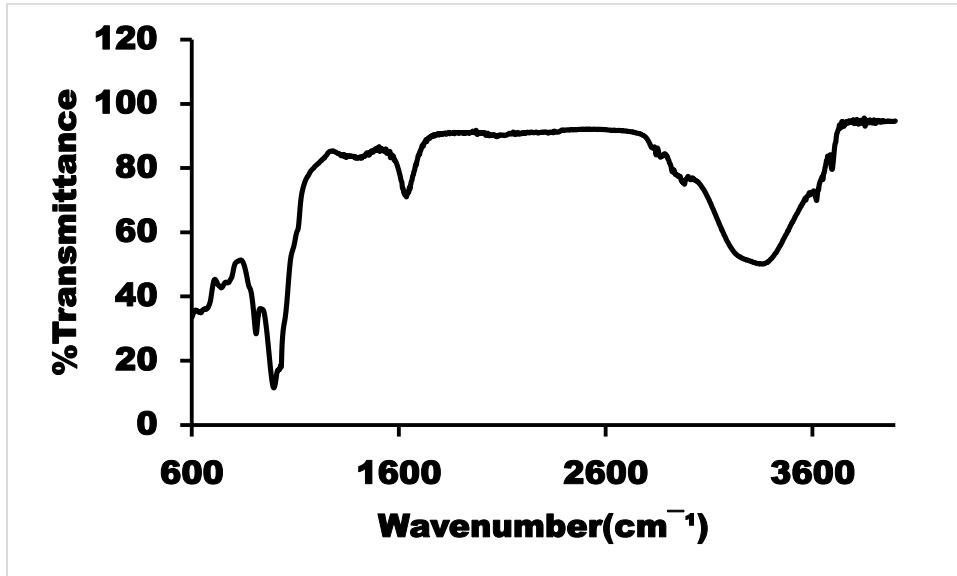


Figure 4:3 FT-IR spectrum of C-B-nZVI

#### 4.2 Batch Study

##### 4.2.1 Effect of nZVI amount in sample on caffeine adsorption

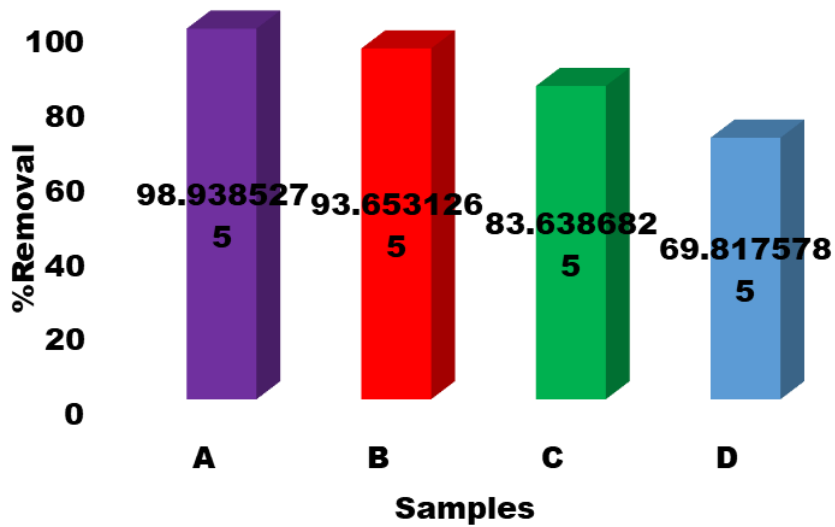


Figure 4:4 Effect of ZVI amount on caffeine removal

4.2.2 Effect of C-B-nZVI dosage on caffeine removal

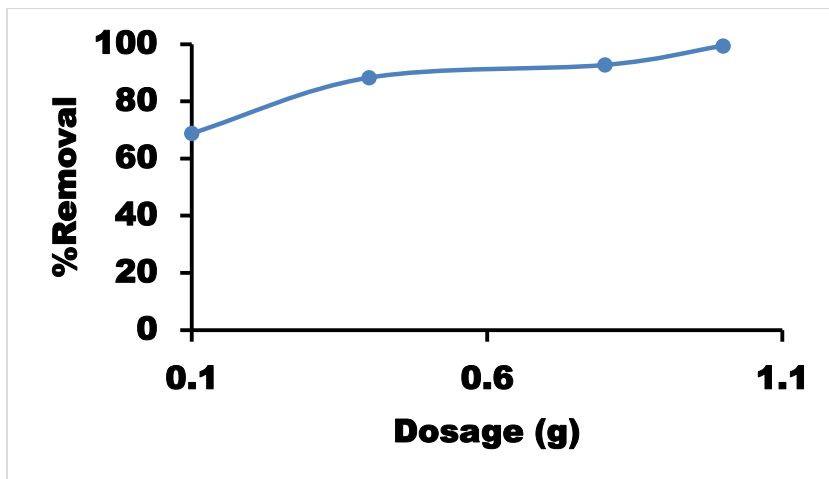


Figure 4:5 - Effects of adsorbent dosage on caffeine removal

4.2.3 Effect of pH on caffeine removal

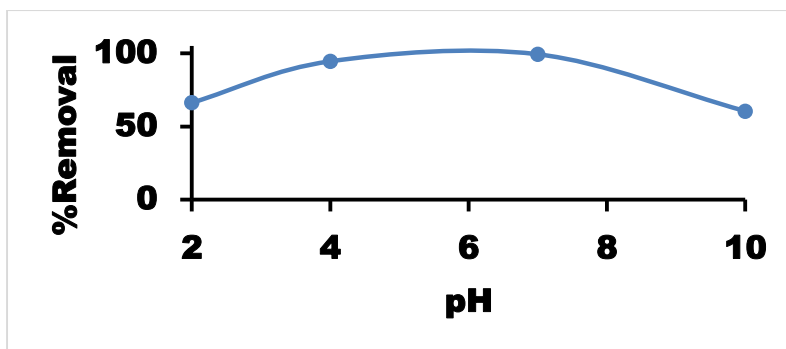


Figure 4:6 Effect of pH on caffeine removal

#### 4.2.4 Effect of initial caffeine concentration on adsorption

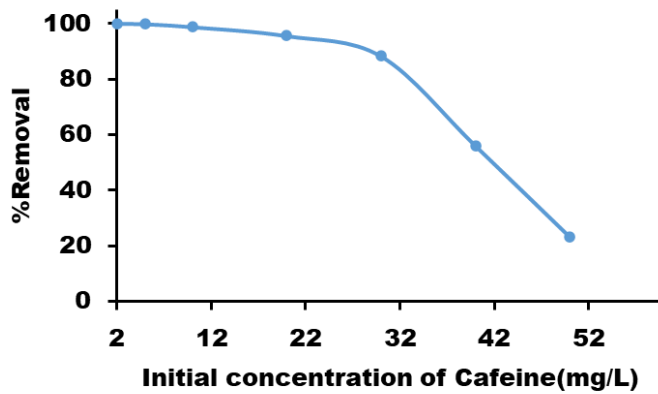


Figure 4:7 Effect of initial concentration on caffeine removal

#### 4.2.5 Effect of temperature on caffeine removal

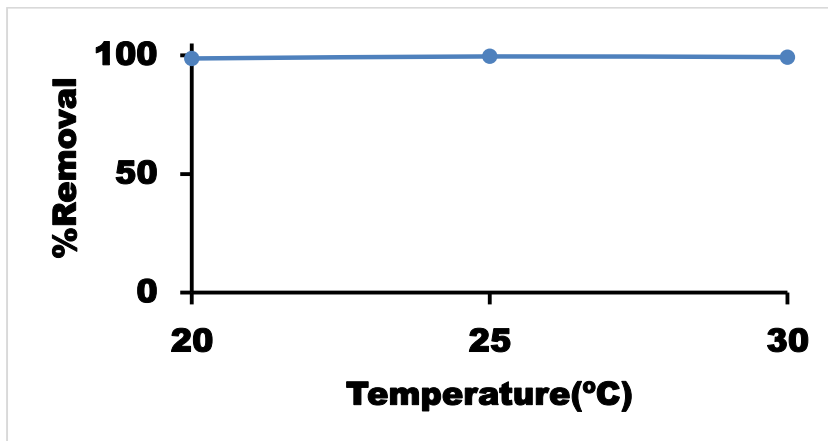


Figure 4:8 Effect of temperature on caffeine adsorption

#### 4.2.6 Effect of contact time on caffeine adsorption

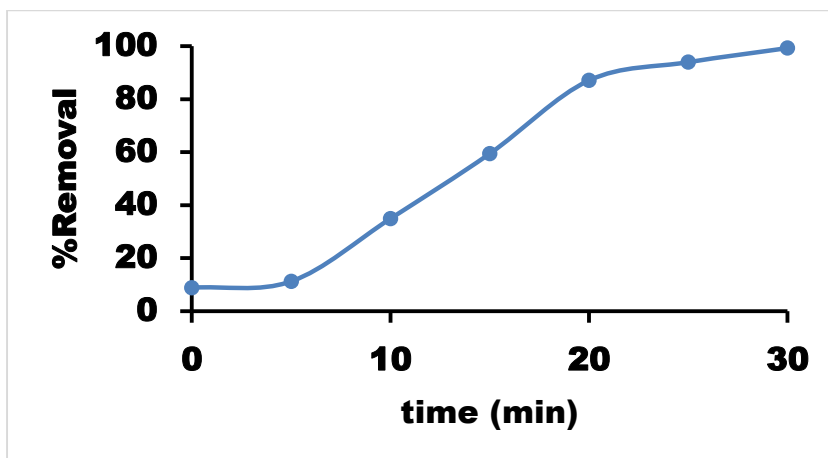
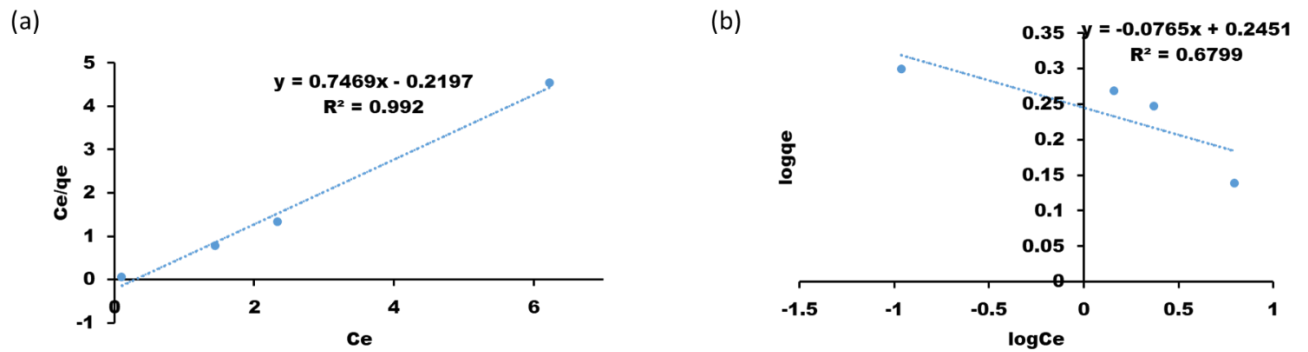


Figure 4:9 Effect of contact time on caffeine adsorption



### 4.3 Adsorption Isotherms

#### 4.3.1 Langmuir and Freundlich adsorption isotherms



**Figure 4:10** Langmuir(a) and Freundlich(b) isotherms

**Table 4.1** - Isotherm parameters for adsorption of caffeine on C-B-nZVI

Langmuir	$q_m$ (mg/g)	1.339
	$K_1$ (L/mg)	0.999
	$R^2$	0.992
Freundlich	$K_f$	1.758
	$n$	-13.157
	$1/n$	-0.0767
	$R^2$	0.6799

#### 4.4 Adsorption Kinetic studies

##### 4.4.1 Pseudo first and second order kinetic models

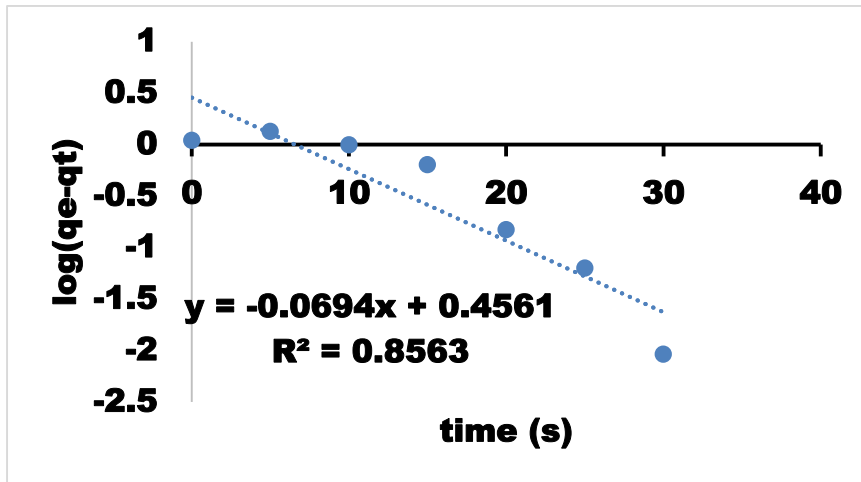


Figure 4:11 Pseudo first order kinetic plot

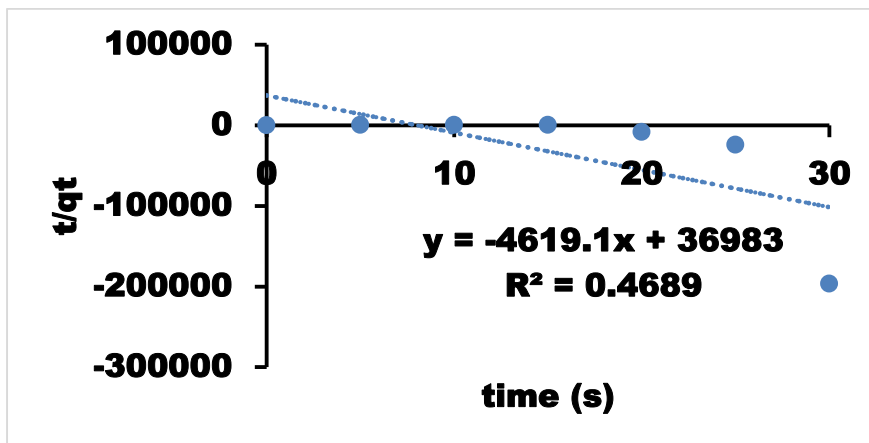
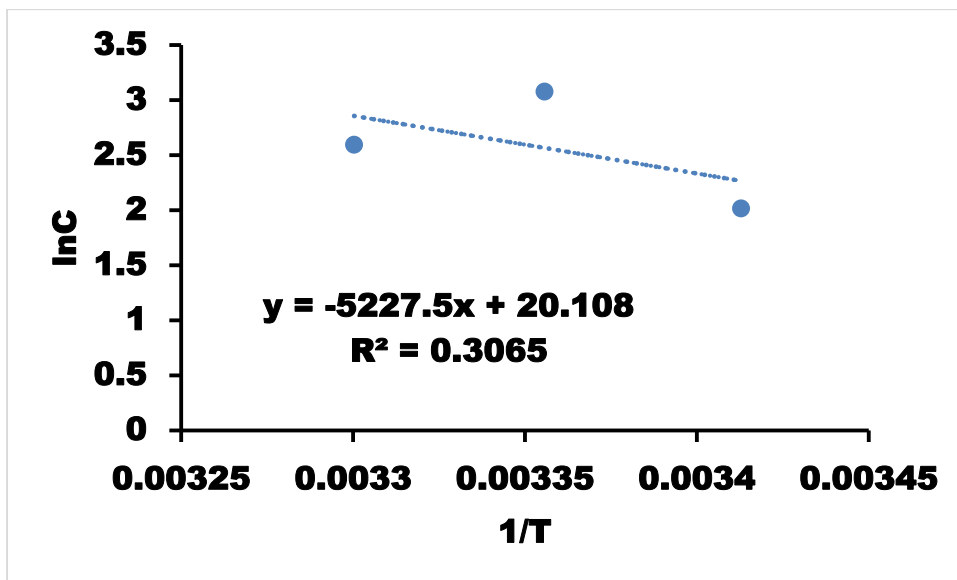


Figure 4:12 Pseudo second order kinetic plot

**Table 4.2** - Parameters for the pseudo first and second order models

Model	Parameter	Results
Pseudo First order	$Q_e$	2.858
	$K_f$	0.159
	$R^2$	0.8563
Pseudo Second order	$Q_e$	
	$K_2$	-0.0002
	$R^2$	0.4689

#### 4.5 Adsorption thermodynamics



*Figure 4.13* Adsorption thermodynamics

**Table 4.3** Parameters for adsorption thermodynamics

T, K			
318	-3436.7	-43 461.4	167.178
323	-3671.3		
328	-3894.4		

## **CHAPTER 5: Discussion**

### ***5.1 Characterisation of the samples***

The FTIR spectra for BC, clay and ZVI-CLAY-BC composite are shown in Fig 4.1- 4.3. A band at  $3437\text{ cm}^{-1}$  that denotes to O–H stretching vibration; a band at  $1636\text{ cm}^{-1}$  that denotes to O–H bending; and from surface water. The band at  $674\text{ cm}^{-1}$  that denotes to stretching vibration of Fe–O from the oxide layer of the ZVI due to oxidation. A characteristic band at  $1002\text{ cm}^{-1}$  corresponded to Si–O–Si in silicate groups in clay. The peak around  $2100\text{ cm}^{-1}$  for BC suggested the presence of C=C stretching of an alkyne also exhibited a peak at  $1743\text{ cm}^{-1}$  which can be attributed to the presence of C=O stretching and peaks at  $2861\text{ cm}^{-1}$  for BC suggested the presence of C-H of an alkane.

### ***5.2 Batch Study***

#### ***5.2.1 Effect of ZVI amount in sample on removal of caffeine***

The effect of the amount of ZVI in sample on Caffeine adsorption efficiency was investigated at initial Caffeine concentration of  $20\text{ mg/L}$ , room temperature and contact time of 30 minutes and varied C-B-nZVI samples with ratios of ZVI:Clay:Biochar as follows sample A 1:0.5:0.1, sample B 1:0.3:0.1, sample C 0:1:0.2, sample D 1:0.1:0.1. Adsorption efficiency was highest for sample A at 98.94 % and least for sample D at 69.82 % as shown on fig 4.4. The high adsorption of sample A is due to the biochar and clay support material which increase surface area of the C-B-nZVI composite and the porous structure as well. Also, the high adsorption of caffeine on sample A show that the ZVI and clay were combined in proper impregnation ratio leading to formation of optimum active sites on the composite were as a decrease in clay in sample B resulted in decrease in adsorption to 93.65 %.

#### ***5.2.2 Effect of adsorbent dose on Caffeine removal***

The effect of mass of adsorbent on the adsorption of Caffeine was investigated. Different amounts of the C-B-nZVI were used which ranged from  $0.1\text{ g}$  to  $1\text{ g}$  at room temperature using a  $20\text{ mg/L}$  Caffeine solution. Adsorption capacity increased from 64.70 to 98.60 % with increase in adsorbent dose as clearly shown on fig 4.5. At low adsorbent mass adsorption is very low due to a small surface area hence fewer sites for the caffeine to adsorb, adsorption increased gradually with increase in mass of adsorbent as more sites were available for adsorption of Caffeine till equilibrium was reached. The equilibrium was due to active sites overlapping each other at very high dose of  $1\text{ g}$  of the adsorbent as well as aggregation. An

increase in mass of adsorbent resulted in an increase in adsorption of caffeine because adsorption mainly occurs on the adsorbent's surface. Similar results were obtained for caffeine removal from aqueous solution by natural clay adsorbent sepiolite where an increase in mass of adsorbent increased breakthrough and exhaustion times as more binding sites became available (Sotelo et al., 2013).

### *5.2.3 Effect of pH on caffeine removal*

To investigate the effect of pH on removal of caffeine from solution at room temperature, 20 mg/L Caffeine solution, and 1 g of adsorbent, the pH of the solutions was varied from 2-10. 0.1M HNO<sub>3</sub> or NaOH were used to adjust the different solutions, as illustrated in fig 4.6 adsorption of caffeine from solution dropped from 63.40 to 59.97 as the pH was increased from 2 to 10 which is from acidic pH to basic pH. From pH 2-4 there was a sharp increase in % removal of caffeine from solution, thereafter from pH 4-7 there was a slight increase in % removal of caffeine from solution. From pH 7-10 the % removal of caffeine from solution dropped sharply, altering pH affects surface properties of the adsorbent thus influencing the competition for binding sites by ions, hence it determines the degree of adsorption of the adsorbate on the adsorbent surface. The relative effect of pH on caffeine removal from water is determined by the concentrations of the OH<sup>-</sup> and H<sup>+</sup> ions, when the solution is acidic the H<sup>+</sup> dominates the surface of the used adsorbent whilst in an alkaline environment the OH<sup>-</sup> will dominate the caffeine ions as there is direct competition for adsorption sites. As a result of the hydrogen ions and hydroxyl ions domination of the adsorption sites the sorption of caffeine cations and anions is greatly reduced thus an extremely low and high pH reduced adsorption of caffeine ions on the C-B-nZVI. The same trend was observed in other research (Sotelo et al., 2014).

### *5.2.4 Effect of initial Caffeine concentration on adsorption*

To investigate the effect of initial concentration on caffeine adsorption at room temperature, 1 g of adsorbent, 180 rpm and a pH of 4.6 various caffeine solutions of 2 mg/L, 5 mg/L, 10 mg/L, 20 mg/L, 30 mg/L, 40 mg/L and 50 mg/L, were prepared using serial dilutions. As shown by fig 4.7 above there was a slight decrease in % removal from 100-90.2 between 2 mg/L and 30 mg/L, from 30-50 mg/L there was a more significant drop in % removal of Caffeine from solution from 90.2-20.0 %. The decrease in % removal of caffeine solution between the concentrations of 2-30 mg/L was not very significant. The removal of caffeine from its solution decreased with increase in initial concentration, this was a result of the caffeine molecules

quickly occupying active sites for the small dosage. The high uptake of caffeine at low concentrations was due to availability of more active sites for lesser number of adsorbate species. Other studies have shown that higher initial caffeine concentration led to decrease in mass transfer resistance, thus the adsorbent achieved saturation more quickly and exhaustion time was decreased (Sotelo et al., 2013).

#### *5.2.5 Effect of contact time on the removal efficiency of caffeine*

The effect of the amount of time required for maximum removal of Caffeine from solution using C-B-nZVI was investigated at temperatures 20, 25 and 30 °C, initial caffeine concentration of 20 mg/L and varied contact time which ranged from 0- 30 minutes. Adsorption efficiency increased from 11.03 to 100 % with an increase in contact time between the C-B-nZVI and caffeine solution as illustrated on fig 4.9, a steep increase in adsorption was observed between 5-20 minutes. Increasing contact time gives pollutants more opportunities to attach to the surface of the adsorbent and results in a more complete adsorption equilibrium (Nam et al., 2014). From 20-30 minutes a small increase in adsorption was observed as equilibrium had been reached. The less significance in % removal between 20-30 minutes was due to saturation of active sites as equilibrium had been reached.

#### *5.2.6 Effect of Temperature on Caffeine removal*

To investigate the effect of temperature on the adsorption of the caffeine from solution 1 g of C-B-nZVI and 180 rpm using 20 mg/L of caffeine solution different temperatures of 20 °C, 25 °C and 30 °C were used. As indicated on fig 4.8 the % removal of caffeine from solution was constant with an increase in temperature. The temperature is a crucial factor among the controlling parameters of the extent of the adsorption of organic contaminants onto mineral surfaces. Depending on the adsorption mechanism, the temperature has reverse effects. Physical adsorption is an exothermic process and hence is generally considered to be enhanced at lower temperatures, whereas the impact of temperature of ionic exchange is still debated. Several studies were conducted on the impact of temperature on the adsorption capacity of PPs on natural clays. An aggregation of these results shows that physical adsorption, mostly for the adsorption of neutral and anionic PPs onto clay minerals, is enhanced for lower interaction temperatures as the solid/water partition is higher for lower temperatures, whatever the adsorbent (Thiebault et al., 2020).

### **5.3 Adsorption Isotherms**

The linear forms of the Langmuir and Freundlich models were adopted in order to determine the model which was best fitted by adsorption, the Langmuir model assumes that adsorption only happens on a single layer, surfaces and sites are homogenous and the adsorption heat is independent of surface closure (Iryani et al., 2017). On the other hand, the Freundlich isotherm assumes the adsorbent has a heterogeneous surface and that each molecule has different potential of adsorption (Iryani et al., 2017).

*Figure 10a and 10b* shows the Langmuir and Freundlich adsorption models respectively for the adsorption of caffeine on C-B-nZVI. Adsorption followed the Langmuir model to a larger extent as compared to the Freundlich model as depicted by the  $R^2$  values. The correlation factor ( $R^2$ ) for the Freundlich model was 0.6799 and that of Langmuir was 0.992. The slope for the Langmuir isotherm is used to measure adsorption capacity. The value obtained for the study was 0.7469 which means the adsorption occurred on a specified surface of homogeneous adsorbents thus it favored the Langmuir model. The surface of adsorbent was homogeneous thus a monolayer was formed during the adsorption experiments. *Table 4.1* shows the isotherm parameters for adsorption of caffeine on C-B-nZVI.

### **5.4 Adsorption kinetic studies**

#### **5.4.1 Pseudo first and second order kinetic models**

*Figure 4.11 and 4.12* illustrates the Pseudo first and second order models. As illustrated in *table 4.2* the correlation factor ( $R^2$ ) for the pseudo first order plot was 0.8563 which was more than that of the pseudo second order which was 0.4689. Adsorption favored the pseudo first order model (Saleh, 2015)(Iryani et al., 2017).

#### **5.5 Adsorption Thermodynamics**

As shown in *table 4.3*  $\Delta G^\circ$  values were all negative for the different temperatures which indicate that the reactions were spontaneous, thermodynamically. The positive value for entropy indicates that the degree of freedom of the particles of the adsorbate found in the solid-liquid interface during the process of adsorption is very high. The negative value for  $\Delta H^\circ$  resembles an exothermic reaction (Saleh, 2015).



## ***5.6 Conclusion***

The results of the study show that clay, and biochar can be used successfully as support materials for nano zerovalent iron to prepare C-B-nZVI composite that can be used as an adsorbent to remediate water from emerging organic micropollutants such as caffeine. The study clearly revealed that efficient adsorption depended on an optimum pH of 7, adsorbent dosage of 1 g and contact time of 30 minutes. The adsorption data when fitted to Langmuir and Freundlich adsorption isotherms best fitted the Langmuir model. The correlation factor ( $R^2$ ) for the Freundlich isotherm was 0.6799 and for the Langmuir isotherm was 0.992 which means adsorption best favored the Langmuir model. Adsorption kinetics best fitted the pseudo first order. The correlation factors ( $R^2$ ) were 0.8563 and 0.4689 for the pseudo first and second kinetic models respectively.

## ***5.6 Recommendations***

- C-B-nZVI made from clay, biochar and nano zerovalent iron can be used in removal of pharmaceuticals and personal care products from water bodies.
- Regeneration of adsorbent molecules should be explored.
- The effect of adsorbent surface and adsorbent particle size on sorption of organic micropollutants should be investigated.

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