# 3D-PRINTED GEOPOLYMERS FOR ADSORPTION OF CARBAMAZEPINE REMOVAL

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Master's Programme in Chemical Engineering and Water Treatment

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ABSTRACT

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Water is a necessary component of biological life. However, the quality of water has deteriorated due to a variety of factors especially pollution caused by dyes, chemicals, heavy metals, medication, personal care products, pharmaceuticals, pesticides, and surfactants. Pharmaceutical waste is a global problem owing to its enormous influence on the biological community and has been classified as an emerging contaminant.

Carbamazepine is a pharmaceutical medication that is often used to treat depression, PTSD, RLS, diabetic neuropathy, and pain. The quantity of carbamazepine in wastewater is growing as a result of its widespread usage, which has a detrimental effect on both living organisms and humans.

Various traditional and advanced technologies have been used to eliminate this pollution, but they all have certain limits. This thesis study utilized adsorption technology in conjunction with additively manufactured adsorbents as a novel approach to purify wastewater.

This thesis work includes the fabrication of a 3D printed geopolymer adsorbent utilizing activated carbon and hydrotalcite, as well as the execution of batch adsorption studies to determine removal efficiency and the analysis of kinetic and isotherm properties. As a result, 3D-printed adsorbents were found highly potential in studied application.

# ACKNOWLEDGEMENTS

The day has finally here, and I have completed my thesis! I'm overwhelmed with gratitude, excitement, relief, and most importantly, pride in myself. I feel that the greatest achievements in life are made possible via the support and assistance of others, as no one can truly explore the world alone. This is also true for this thesis, and indeed for my entire time in Finland. I'd want to express my gratitude to LUT University for delivering such excellent instruction. Not only did this university give me with an excellent education, but it also assisted me in discovering my true calling in life.

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I'm eager to put this trip behind me and go on a new one.


Papia Yasmin

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## SYMBOLS AND ABBREVIATIONS

Roman characters

| | | |
|---|---|---|
| $p$ | pressure | [bar, Pa] |
| $R$ | gas constant | [J/kg K] |
| $T$ | temperature | [ºC, K] |
| $q_e$ | Equilibrium quantity of the adsorbate | [mg/g] |
| $C_e$ | Equilibrium concentration of the adsorbate | [mg/L] |
| $K_L$ | Langmuir constant | [L/mg] |
| $q_m$ | Maximum adsorption capacity | [mg/g] |
| $K_F$ | Freundlich exponent | [mg/g] |
| $n$ | Freundlich constant | |
| $K_s$ | Sips isotherm model constant | [L/g] |
| $A_T$ | Tempkin isotherm's equilibrium binding constant | [L/g], |
| $b_T$ | Tempkin isotherm constant | |
| $B$ | Adsorption heat constant | [J/mol] |
| $q_t$ | Quantity of adsorbent adsorbed at a time t | (mg / g) |
| $K_1$ | First-order rate constant of adsorption | [1/min] |
| $t$ | Time | min |
| $K_2$ | Second-order rate constant of adsorption | [1/min$^2$] |
| $a$ | Initial adsorption rate constant | [ mg/g.min] |
| $b$ | Desorption rate constant | [mg/g.min] |

Greek characters

| | | |
|---|---|---|
| $\alpha_s$ | Sips isotherm model constant | [L/g] |
| $\beta_s$ | Sips isotherm exponent | |

Abbreviations

| | |
|---|---|
| ABS | Acrylonitrile butadiene styrene |
| AM | Additive Manufacturing |
| AOPs | Advanced Oxidation Processes |
| API | Active Pharmaceutical Ingredient |
| CAD | Computer Aided Design |
| CBZ | Carbamazepine |
| CIJ | Continuous Inkjet |
| DED | Directed Energy Deposition |
| DES | Diethylstilbestrol |
| DOD | Drop on Demand |
| EC | Electrochemical |
| MJ | Material Jetting |
| GAC | Granular activated carbon |
| IUCN | International Union for Conservation of Nature |
| NF | Nanofiltration |
| PAC | powdered activated carbon |
| PFO | Pseudo-first-order model |
| PLA | Polylactic Acid |

PPCPs        Pharmaceuticals and Personal Care Products

PSO          Pseudo-second-order model

RO           Reverse Osmosis

STP          Sewage treatment plant

UN           United Nation

US EPA       United States Environmental Protection Agency

WWTPs        Wastewater Treatment Plants

3D           Three-dimensional, or having three dimensions

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# 1. Introduction

Water is the most essential element for the survival of all living organisms on the planet, including humans. However, water quality is deteriorating, resulting in a global lack of safe water resources. Water-soluble dyes (WSB), heavy metals, and emerging contaminants including any synthetic or naturally occurring chemicals for instance, medicines, personal care products, pesticides, endocrine-disrupting substances, surfactants, and herbicides damage the water resource due to rising industrialization and urbanization (K, AA and D, 2006; C et al., 2009; Stuart, 2011; G et al., 2014). The number of pharmaceutical effluents in the water body increases as the demand for pharmaceuticals increases. These drugs remain resistant to standard WWT technologies.

Initially, this issue received attention in the Western world, particularly in the United States, Canada, and Europe. In 1990, German environmental scientists published the first report on pharmaceutical detection following the discovery of clofibric acid, a cholesterol-lowering medication, in groundwater beneath a water treatment facility. This was the first report of medication detection. Then, in the mid-1990s, another German scientist, Thomas Ternes, began looking into the long-term effects of prescription medications. Every day, more research of wastewater-containing medicines is conducted, and the importance of this is becoming increasingly apparent. Earlier in 2016, it was discovered that up to 95% of prescription medication dosages were removed from the body in their original form in sewage. The great majority of STP were not intended to be used to remove medicines throughout the study period. Despite the widespread acknowledgment of pharmaceutical pollution of waterbodies, pharmaceutical control guidelines and regulatory requirements was not implemented effectively (Quevauviller et al., 2005). PPCPs are discharged into the environment constantly. Because of their widespread use at low concentrations (T and T, 2005), the vast majority of PPCPs continue to be life-threatening to humans and hazardous to the environment (Kyzas et al., no date; OA, JN and N, 2005). The feminization of aquatic species in the vicinity of wastewater treatment plants is an example of this phenomenon (Kyzas et al., no date).

Pharmaceutical drugs are classified based on their pharmacological activity and the length of time they are expected to be effective. The term "API" refers to molecules that are able to construct massive complexes with diverse functionalities, molecular weights, structures, and shapes in aquatic environments. Carbamazepine is an example of an active pharmaceutical ingredient (API) that does not breakdown or become adsorbed throughout the wastewater treatment process (Bonnineau, C., Moeller, A., Barata, C., Bonet, B., Proia, L., Sans-Piche, F., Guasch, H., Segner, 2012). Carbamazepine ($C_{15}H_{12}N_2O$) is a commonly recommended anti - epileptic medicine used to treat depression, PTSD, RLS, diabetes, pain, and neurological disorders (MN and B, 2012). Earlier research estimated that globally the annual CBZ consumption is roughly 1010 tons. Due to widespread use of CBZ, it has been detected in almost all waterbodies which include surface and groundwater, WWTPs, and sometimes in potable water. Thus, the occurrence of CBZ in various water sources has been viewed as a worldwide problem (Y, SU and C, 2008). CBZ has been documented to have harmful impact on microorganisms lived in water, namely bacteria, algae, crustaceans, and fish (B et al., 2003). The standard concentration of CBZ in drinkable water supplies differs from country to country and the restriction is 40 μg/kg for Minnesota, US, and 100 μg/kg for Australia (Hai et al., 2018). Furthermore, the application of CBZ-containing water for watering soil leads to the soil accumulation (KINNEY et al., 2006). Recommended limit of CBZ in wastewater-irrigated soils range from 0.02–15 μg/kg (F et al., 2011). As per United states guidelines, If the quantity of CBZ active ingredient is equal to or exceeds 1.0 μg/L in aquatic environment, an environmental evaluation should be done (Hai et al., 2018). It is therefore necessary to develop effective treatment solutions in order to rid aquatic environments of this contaminant.

Numerous methods for removing medicinal compounds from water on an as-needed basis have been developed where some of the predeveloped method was utilized for removing pharmaceutical compounds, including aerobic and anaerobic microbial degradation, coagulation-flocculation, membrane separation, electrochemical process, flotation, filtration, precipitation, AOP, and RO, each of which has its own set of benefits and drawbacks (Robinson et al., 2001). Alternative solutions are required in order to successfully eliminate these contaminants while retaining the process's economic feasibility and efficiency.

Adsorption has recently been shown to be an efficacious and relatively economical approach for the treatment of persistent pollutants (Akhtar, Amin and Shahzad, 2015). Adsorption of various aquatic contaminants has been studied using clays, polymers, and carbon-based compounds (including fly-ash or charcoal) Moreover, activated carbon has garnered considerable interest (Marrero-Rivera Adam Johnson et al., 2018) owing to its large surface area and superior chemical and mechanical characteristics. However, the activation process is complex and expensive. Since 1990s, geopolymer-based adsorbents have become increasingly popular due to their low cost, rapid strength, and environmental friendliness, as well as their non-reactivity with hazardous pollutants, high ion exchange efficiency, and capacity to more efficiently solidify toxic waste (Lertcumfu et al., 2020a).

Additive manufacturing is a bundle of emerging strategy that utilize digital model to produce 3D printed object by depositing material layer-by-layer. The use of AM technology is grown up recently in a variety of industries, including biomedical, consumer & food, automotive, aerospace, and construction. For the adsorption technology, additive manufacturing technique provides easier handling procedure, mechanical stability, wide surface area by providing more active sites for adsorption, precise porosity for increasing adsorption capacity due to pore diffusion, enhanced fluid dynamics owing to optimized channel structure and better contact between water and surface. These properties are vital for ideal adsorbent materials that is why AM technology is gaining popularity for adsorption processes ('Additive manufacturing-General principles-Terminology', 2015)

The goal of this research is to analyse CBZ removal strategies, as well as the capability of 3D printed geopolymer in comparison with milled composite of AC and geopolymer, milled composite of hydrotalcite and geopolymer and 3D printed AC fabricated geopolymer for the efficient removal of CBZ. Batch experiments were required to ascertain the influence of critical experimental variables on the adsorption process. Following the collection of data from batch testing, research was conducted to build isotherm and kinetic models, as well as to determine the adsorbents' sorption and desorption capacities.

Fourier transform infrared (FTIR) was used to analyse the surface functionalities of the studied materials.

# 2.     Pharmaceutical compounds in water

Recognition and distinguishing of pharmaceuticals as emerging contaminants in aquatic habitats have already been identified as being one of the most critical ecological problems in recent decades. Medicines are a broad and diversified category of substances that are used to protect, heal, and diagnose diseases, as well as to enhance overall health and well-being. Over 3000 distinct PhACs have been authorized to be used for treating human along in the EU. Due to the rising demand of these chemicals, considerable amounts of such chemicals have been detected in aquatic environments, and treated sewage and industrial effluents.

## 2.1     Global Pharmaceutical Occurrence

Over the course of last eighty years, it has been known that both the naturally derived and manufactured substances have the power to change the hormonal function of animals' reproductive organs and systems (Cook et al., 1934; Cook, J., Dodds, E., & Greenwood, 1934; Emge and Murphy, 1938). In the 1960s, the United States began receiving allegations of water contamination caused by sophisticated chemical compounds produced for commercial, agro - industrial, and domestic usage. It was discovered in the late twentieth century (1990s) that fish living downstream of wastewater treatment plants were exhibiting reproductive anomalies, including feminization (WWTPs). Even though the pharmaceuticals can act as endocrine disruptors, the first assessment aimed at identifying these substances in drinking water and sewage was conducted in 1965 (Elisabeth Stumm-Zollinger and Gordon M. Fair, 1965). In 1990s, pharmaceuticals were recognized as environmental pollutants when found at trace concentrations in the environment (Halling-Sørensen et al., 1998; Daughton and Ternes, 1999). various researches have documented its occurrence in effluent, sewerage , water bodies and occasionally in drinkable water in countries all over the world, including the United States of America (Kolpin* et al., 2002; Benotti et al., 2008), Germany (Heberer and Stan, 1997; T, K and A, 2002), Italy (Meffe and de Bustamante, 2014), Australia (AJ et al., 2009), China (BJ, PK and M, 2005), South Africa, and Brazil  (M et al., 1999; Ternes et al., 1999; De Almeida et al., 2013; I and WF, 2017). Despite frequent discovery of new pollutants in water bodies, the vast majority of newly discovered

contaminants remain unregulated under current water quality regulations. Priority pollutants lists were first used by the US EPA ('Contaminant Candidate List 4; 81 FR 81099; U.', 2016) and the EU ('European Union, Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008; on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156', 2008), which were both pioneers in the field.

## 2.2 Pharmaceutical pollution scenario

A significant number of pharmaceuticals are discarded in sinks and toilets and end up in the environment. Unwanted pollutants may also be caused by improper and irresponsible use. The advancement of technology allows us to detect pharmaceutical compounds even in a shallow concentration like nano scale to micro scale and their consequence on the environment. More than thousand international publications have proven the presence of 631 different active pharmaceutical compounds, their metabolites, and their transformation products in seventy-one nations belonging to all five UN regional groups of the world. In total, sixteen pharmaceutical substances, ibuprofen, diclofenac, estriol, carbamazepine, norfloxacin, ciprofloxacin, sulfamethoxazole, naproxen, paracetamol, estrone, ofloxacin, trimethoprim, estradiol, ethinylestradiol, clofibric acid, were detected in surface, drinking, and groundwater in these five regions. The mentioned substances belong to the therapeutical groups: Analgesics, Antiepileptics, Analgesics, Antibiotics, Estrogens, and Lipid-lowering drugs. According to the published data, globally averaged values ranged from 0.003 g/L of estradiol to 18.99 g/L of ciprofloxacin. (T et al., 2016). In growing nations such as Brazil, stated average medication amounts in water maybe comparatively high (MA, FF and WF, 2011; Thomas et al., 2014; MB et al., 2015).
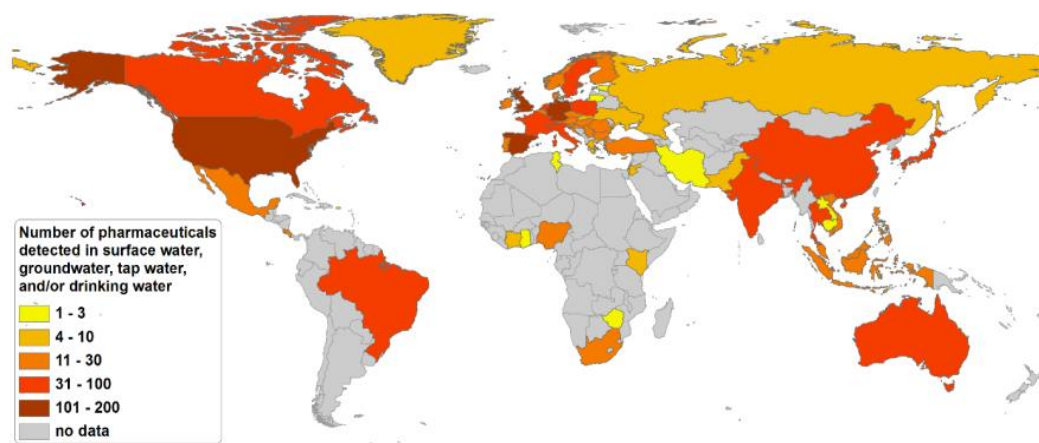
Figure 1. Worldwide distribution of pharmaceuticals: Pharmaceuticals detected in each of the five United Nations regional groups (Weber et al., 2014a)

Carbamazepine (CBZ) (5H-Dibenz azepine-5-carboxamide) as neutral antiepileptic drug is among the most frequently reported pharmaceuticals in surface waters observed at a concentration more than ten times higher than other micropollutants due to its high persistency. Although most observations have been reported in developed nations, revealing the worldwide scope of medicines in the environment and monitoring programs in underdeveloped and emerging countries are progressively being performed. For example, Diclofenac, anti-inflammatory medicine, used to reduce inflammation and mild-to-moderate pain, has been found in the water bodies in 50 countries worldwide. Figure 2 also depicts the use of 4 other well-known pharmaceuticals, which were found in the five UN region. The difference in drug appearance depends on several factors like the waste treatment process and accessibility for buying medicines.

**Pharmaceuticals found in each UN region**

| | Diclofenac | Carbamazepine | Ibuprofen | Sulfamethoxazole | Naproxen | Estrone | Estradiol | Ethinylestradiol | Trimethoprim | Paracetamol | Clofibric acid | Ciprofloxacin | Ofloxacin | Estriol | Norfloxacin | Acetylsalicylic acid |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Global | 50 | 48 | 47 | 47 | 45 | 35 | 34 | 31 | 29 | 29 | 23 | 20 | 16 | 15 | 15 | 15 |
| WEOG | 23 | 24 | 24 | 21 | 23 | 16 | 17 | 17 | 13 | 15 | 12 | 11 | 9 | 10 | 7 | 7 |
| GRULAC | 3 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 3 | 2 | 2 | 1 | 1 | 2 | 2 |
| EEG | 13 | 13 | 10 | 10 | 10 | 6 | 4 | 3 | 3 | 4 | 5 | 1 | 1 | 2 | 1 | 1 |
| Asia Pacific | 8 | 6 | 8 | 9 | 8 | 10 | 9 | 8 | 9 | 6 | 3 | 5 | 4 | 1 | 4 | 4 |
| Africa | 3 | 3 | 3 | 5 | 2 | 1 | 2 | 1 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |

Figure 2. The number of countries in all UN regional groups where drugs have been detected in the aquatic environment.(Weber et al., 2014a)

Wastewater undergoing treatment has a lower concentration ranging from 0.1 µg/L - 1.0 µg/L whereas increased concentration might be found in inhabited areas or descending of Sewage treatment plant (STP). Although there is little information on medicines in manure and soil, twenty-eight countries have identified leftovers, particularly in areas where intensive livestock ranching is conducted.

2.3        Route of pharmaceutical entry in water

There are a variety of intricate routes through which pharmaceutical residues might reach the water as illustrated in Figure 3. It was discovered that wastewater from pharmaceutical manufacturing facilities has a high concentration of compounds generated during the manufacturing process (Larsson, de Pedro and Paxeus, 2007). Following the manufacturing step, pharmaceutical items are distributed to pharmacies, healthcare facilities, and ultimately to users. To cure and prevent diseases, the majority of medications are used in hospitals, healthcare facilities, as well as by individual customers and agriculture (particularly farming and animal husbandry). Pharmaceutical compounds are digested to varying degrees by the body when eaten by humans or animals. Their metabolites and parent (original) chemicals are excreted in urine and feces that are then disposed of in the sewage system. Following that, different type of processes (physical, chemical and biological) occurring within WWTPs and aquatic environment might further modify the structure of these chemicals (D, S and A, 2011; Deblonde, Cossu-Leguille and Hartemann, 2011).
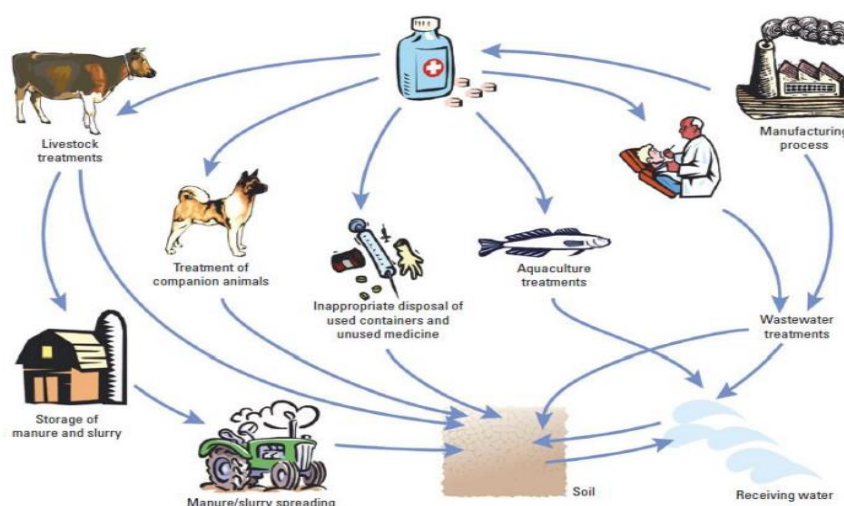


Figure 3. PPCPs' routes of entry into the aquatic environment (Boxall et al., 2012)

Through surface runoff, farm animal feces may be exposed to the upper soil layer and surface water. The pharmaceutical metabolites and parent (original) chemicals of the feces may persist in the soil layer or seep into the groundwater system (Deblonde, Cossu-Leguille and Hartemann, 2011). Additionally, hospitals are a source of pharmaceutical discharge. Due to

the fact that hospitals do not typically have a sewage water treatment plant on-site to treat their effluents immediately after discharge, a significant proportion of chemicals generated by healthcare services are discharged straight into urban wastewater (T et al., 2016). Numerous medications were detected in significant amounts in the sewage discharge from a hospital (F and Y, 2013).

Most municipal WWTPs were built to eliminate biodegradable carbon, nitrogen, phosphorus, and microorganisms, rather than complex pharmaceutical residuals. The clearance rates of the majority of chemicals range between 20% and 80% (Weber et al., 2014b). It is not, however, complete removal, as pharmaceuticals find up in receiving waters when effluent from WWTPs is discharged. They can then build up in bodies of water, soil, groundwater, and drinking water, and eventually in living creatures.

# 3.　　　Technologies for pharmaceutical removal

Numerous drugs are not entirely eliminated during WWT and are not readily biodegraded when released into the environment (McEniff, Schmidt and Quinn, 2015). Examples of pharmaceuticals that have been observed to be inadequately eliminated in WWTPs include naproxen, clofibric acid, carbamazepine, and ketoprofen (Baccar et al., 2012). As a result, alternate WWT approaches are required to reduce the potential effects of these contaminants (Salamatinia B, 2015). The fundamentals of the numerous traditional procedures that can be employed to remove pharmaceuticals from aquatic systems are outlined in further detail below

## 3.1　　　Chemical precipitation

A chemical precipitation technique, sometimes called reagent coagulation, is a method of removing organic pollutants such as phosphorus containing drugs from treated wastewater by modifying the pH, increasing the electro-oxidizing potential, or co-precipitating them with coagulants such as ferrous or aluminium sulphates.(Sun et al., 2017) Chemical precipitation is usually accomplished in following stages: reagent addition, pH adjustment to produce the precipitate, flocculation, sedimentation, and solid-liquid separation. Chemical precipitation is a straightforward method of wastewater treatment. Powerful alkaline reagents have typically been used to elevate the pH of the wastewater. This causes soluble pollutants to convert into insoluble hydroxide, carbonate, or sulphide forms, which then deposit in an alkaline environment. Chemical precipitation, by its very nature, results in the creation of sludge, and as a result, it must be used in conjunction with physical procedures for separating the sludge from the supernatant fluid. (USEPA, 2000) In the process of sedimentation, wastes are contained in a tank, and gravity is used to remove suspended solid particles from the solution at a pace determined by Stokes' Law. (Ojovan, Lee and Kalmykov, 2019) The efficiency of the process is influenced by the kind of metal utilized, its concentration, and the type of reagent employed. However, conventional reagents have a number of drawbacks, including the fact that the majority of sulphide reagents in an acidic solution can produce hazardous hydrogen sulphide gas, which is harmful to human health

and the environment. In addition, powerful alkaline precipitating agents are corrosive to laboratory equipment. Due to this, experts are looking for a weak alkaline reagent that is both affordable and non-corrosive.(USEPA, 2000)

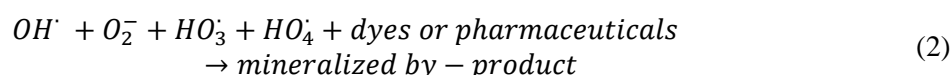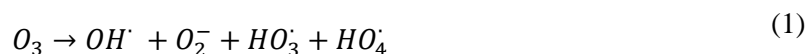## 3.2 Coagulation-flocculation

Coagulation-flocculation can be employed as a preliminary step in the removal of medicinal substances. Coagulation–Flocculation is a process in which coagulants such as metal salts (such as calcium chloride, aluminum sulphate), polymers (such as polymeric aluminum sulphate, polyaluminium chloride, and polyaluminium chloride sludge) or other naturally occurring materials reduce or neutralize the surface charge of dispersed particles, and flocculants such as polymers aggregate to form large particles. However, the majority of drugs are organic in nature and so cannot be absorbed by coagulants. Coagulation can remove only 3% of drugs from the total contaminant load (Lertcumfu et al., 2020b). Additionally, this process is inefficient since it requires additional employees to monitor the pH or other characteristics of the effluent, and it generates more sludge, which requires additional storage and transportation.

## 3.3 Advance oxidation processes (AOPs)

Advanced oxidation processes are divided into many categories based on a few parameters such as the technology utilized, OH production, system type (homogeneous or heterogeneous), and energy supply requirements (required or not required). However, Poyatos et al. categorized the most practical advanced oxidation methods based on the OH production technology as follows: Ozonation, Fenton process, and photo-catalysis (Poyatos et al., 2009)
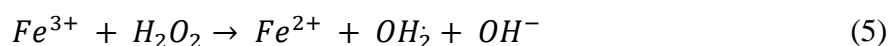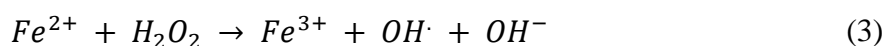
Ozonation: Ozone is a strong oxidant with a high oxidation potential (2.07eV). (Glaze, Kang and Chapin, 2008) The ozone produced by passing air through discharging electrodes is infiltrated into the wastewater to oxidize pollutants. The pollutants like pharmaceutical

compounds oxidize instantly with ozone by direct reactions because of the strong oxidative action of $O_3$ and the rest are oxidized by $OH^{\cdot}$, produced from ozone decay. The occurring reactions are shown in equations (1) & (2) (Umar et al., 2013)

$$O_3 \rightarrow OH^{\cdot} + O_2^{-} + HO_3^{\cdot} + HO_4^{\cdot} \tag{1}$$

$$OH^{\cdot} + O_2^{-} + HO_3^{\cdot} + HO_4^{\cdot} + dyes\ or\ pharmaceuticals \\ \rightarrow mineralized\ by-product \tag{2}$$

Ozonation provides high oxidation rate but still is incapable of breaking down complex organic pollutants. To assure spontaneous oxidation, it is necessary to generate OH radicals, which can be accomplished by using an ozonisation catalyst. The catalyst acts as a radical booster, ensuring continued production of OH radicals by completing the chain reaction. Additionally, it may generate hazardous by-products that are potentially more harmful than the therapeutic molecules (de Souza, Bonilla and de Souza, 2010). Occasionally, ozonation might degrade the unwanted by-products within extending processing time, which adds to the existing operating expense.

Fenton oxidation: Typically, the Fenton reaction uses $H_2O_2$ to generate a hydroxyl radical under the effect of the $Fe^{2+}$ catalyst indicated in Eq. (3) According to Eq. (4) the organic contaminants react with the produced hydroxyl radical, which oxidized a few organic compounds to form organic radicals that continue the oxidation process. During the fast breakdown of $H_2O_2$, ferrous ion converts to ferric ion. Ferric ion reacts with $H_2O_2$ at a slower rate than hydroxyl ion to generate hydroperoxyl radical shown in Eq. (5). Hydroperoxyl radical is capable of oxidizing organic pollutants at a slower rate than hydroxyl ion (Bello, Aziz and Raman, no date).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\cdot} + OH^{-} \tag{3}$$

$$RH + OH^{\cdot} \rightarrow H_2O + R^{\cdot} \rightarrow further\ oxidation \tag{4}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + OH_2^{\cdot} + OH^{-} \tag{5}$$

While the Fenton oxidation stage appears to be relatively straightforward, the actual chain reaction is highly complicated and remains a fascinating subject for investigation. (Hu et al., 2015) The detailed process of Fenton oxidation was discussed before by Neyens and Baeyens.(Neyens and Baeyens, 2003) The homogeneity or heterogeneity of the process is determined by the type of natural catalyst. When soluble $FeSO_4$ is used as a catalyst for decomposing $H_2O_2$, the process identifies a homogeneous system because the $Fe^{2+}$ ion is freely accessible for chemical reactions due to the solution's reduced mass transfer barrier. During the process, it is necessary to maintain a pH range of 2.8-3.5 to ensure the active involvement of $Fe^{2+}$ and $Fe^3+$ and to avoid precipitation of oxyhydroxides, which is a significant disadvantage.(Bello, Aziz and Raman, no date)

## 3.4        Biological Treatment

Using a biological (aerobic or anaerobic) process, various microorganisms such as bacteria, fungi, algae, plants, or enzymes convert biodegradable trash into a harmless form. Carbon - di-oxide, water, and biomass are the end products of aerobic treatment;(Scholz, 2006) while anaerobic treatment produces $CO_2$, $CH_4$, and biomass as end product.(Ahammad and Sreekrishnan, 2016) This method is more environmentally friendly than other methods since it requires less chemical and energy. However, due to the complexity of microbiological mechanisms and the creation of favourable optimal conditions, this process takes extensive attention to sustain the microorganisms (pH, temperature). Certain colours and medicinal compounds have a negligible biodegradability. This process results in the formation of biological sludge and unregulated degradation products. An in-depth grasp of the enzymatic biological process is necessary. (Mayabhate, Gupta and Joshi, 1988) Depending on the treatment technology biological treatment can be classified as activated sludge treatment and membrane bio reactor.(Scholz, 2006)

## 3.5        Electrochemical treatment

Electrochemical treatment of WWs is regarded to be one of the AOPs that has the potential to be a highly effective approach for pollution control due to its high removal efficiency.

Electrochemical procedures often operate at a low temperature, need no extra chemicals, and are relatively simple to implement. The electrochemical process's primary oxidizing agent is hypochlorite ion or hypochlorous acid created from chloride ions.

Electrocoagulation is the primary method of pollution removal in an electrochemical system that employs a sacrificial anode (Ensano et al., 2016). The electrochemical breakdown of the anode produces a variety of monomeric and polymeric metal ion complexes that react with pollutants in the WWs to form flocs that may both destabilize and agglomerate colloidal particles as well as precipitate and adsorb dissolved chemicals (Ganzenko et al., 2014; Elabbas et al., 2016). It is dependent on their physico-chemical properties. An EC system may require the addition of acids or bases in order to achieve the desired pH balance, thus it is not totally additive-free. Additionally, due to the electrode's sacrificial nature in the process, the electrodes will corrode with period, necessitating their replacement.

3.6        Membrane filtration

Membrane filtration is a sophisticated process that results in high-quality end effluents. Membrane filtration is a process in which wastewater is filtered through the membrane's microscopic holes. The bigger solutes cannot pass the membrane and concentration polarization occurs. To maintain a consistent process, the suspended pollutants have to be continuously removed from the membrane. For wastewater treatment, ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), and occasionally a mixture of these filtration processes is utilized. Ultrafiltration, for example, requires less pressure than NF or RO but cannot remove the majority of colours and pharmaceutical contaminants (Suárez et al., 2008). Post-treatment is necessary in the case of UF. While NF and RO are widely utilized in drinking water treatment, their application in wastewater treatment to remove pharmaceuticals is extremely rare. Because these procedures are not economically viable, their use is limited to wastewater treatment (Lu et al., 2007). Recently, a combination of ultrafiltration or nanofiltration with reverse osmosis has been utilized as a post-treatment procedure. Some research indicates that membrane bioreactors are more effective at removing pharmaceuticals from water, as they do not only depend on the size of drugs in

wastewater for treating them (Pharmaceuticals difficult to treat in drinking water | Great Lakes Echo, no date).

3.7        Adsorption technology

Adsorption is a technique for efficiently removing pollutants from effluent streams (Han et al., 2008; V and L, 2011). Adsorption is the process by which a compound from a gaseous or liquid phase is bound on the surface of an adsorbent. Adsorption can occur physically or chemically. Numerous adsorptive materials have been evaluated for their efficacy in removing emerging contaminants like pharmaceuticals eg. Carbamazepine. These include activated carbon (AC) (AS et al., 2009; Guedidi et al., 2013), carbon nanotubes (CNTs) (Bhirde et al., 2010), particularly multi-walled carbon nanotubes (MWCNTs), natural clay materials such as bentonite, ion exchange materials, and biochar (BC). Adsorption experiments are conducted with pharmaceuticals doses up to mg/L, which are typically significantly more than the environmental value (ng/L - μg/L). Specific surface area (SSA), porosity (macro or micro porosity), pore diameter, and functional groups are all important factors in underlying the efficiency of adsorbent (Estevinho et al., 2007). These natural or engineered adsorbents, on the other hand, have a variety of limitations, including economic feasibility, application, effectiveness, and regeneration difficulties, among other things. In this work, drawbacks of adsorption materials are tackled by utilizing tailored geopolymer and activated carbon 3D-structures in the removal of Carbamazepine.

# 4        Adsorption theory

Adsorption is an exothermic mass transfer process that involves the accumulation of molecules of gases or solutes on solid surfaces referred to as adsorbents. The term "adsorbate" refers to the substance that is adsorbed to the adsorbent [12] In contrast to adsorption, desorption is the process by which adsorbed molecules are released from the adsorbent's surface. It is the inverse of adsorption.

(A)

**Adsorbent**

(B)
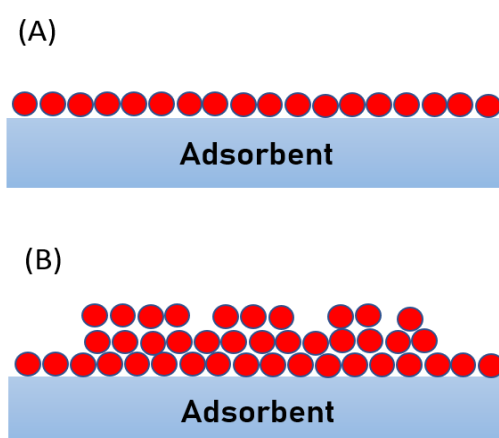
**Adsorbent**

Figure 4. (A) Monolayer adsorption and (B) multilayer adsorption.

The molecules can adsorb to the adsorbent surface in two ways: physically (physisorption) and chemically (chemisorption). This is determined by on molecule-surface interactions. Physisorption is characterized by the involvement of weak forces such as electrostatic interactions and Van der Waals forces. Chemical adsorption is defined by the formation of strong chemical bonds, such as covalent bonds by surface-molecule interaction. Chemical adsorption occurs more slowly than physical adsorption and results in the formation of a monomolecular layer on the adsorbent surface, whereas physical adsorption results in the formation of a thick multilayer [13]. Monolayer and multilayer adsorption on an adsorbent surface is depicted in Figure 4, respectively.

4.1       Adsorption isotherms

A graphical representation of the relationship between the quantity of compound adsorbed on a substrate (a solid) and the quantity of adsorbate left in the solution as a function of the equilibrium concentration (in mg/ $m^2$ or mol/$m^2$) or partial pressure after adsorption at constant temperature is called an adsorption isotherm. Typical graphical representation is $q_e$ (mg/g or mmol/g) vs $C_e$ (g/L or mmol/L). There have been 15 isotherm models established for understanding the adsorption behaviors.(Foo and Hameed, 2010) Understanding adsorption equilibrium is necessary for comprehending any sorption process. The adsorbent's maximum adsorption capacity reveals the efficiency of adsorbent to bind a target component. However, in case of pharmaceuticals the high efficiency value does not matter that much as the detected pharmaceutical's quantity in water is very low (μg/L). Apart from that, isotherms' shape provides information on the adsorbent-adsorbate interaction.

4.1.1       Langmuir isotherm model

Irving Langmuir developed a model known as the Langmuir adsorption model in 1918 for gas-solid system, based on the following statement.

- Adsorption takes place on well-defined localized sites that are confined on the adsorbent's surface.
- On the adsorbent's surface, there are the same number of adsorption sites and one active site only interact with one adsorbate molecule.
- An adsorbent's surface is coated with a monolayer of molecules that have been adsorbed
- Adsorption sites are homogeneous, and the adjacent adsorption site do not interact to one another with the molecules that have been adsorbed on them.

Although the Langmuir isotherm model was developed for the chemisorption process, which involves the formation of covalent or ionic bonds between the adsorbent and adsorbate, it is frequently applied to other adsorption systems and can be expanded to two-component

adsorption processes. (Allen, Mckay and Porter, 2004) Below is the Eq. (6) for the linear Langmuir model:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \tag{6}$$

According to the equation above, $C_e$ in mg/L signifies the equilibrium concentration of the adsorbate, while $q_e$ in mg/g denotes the equilibrium quantity of the adsorbate. The maximum adsorption capacity in mg/g and is represented by $q_m$, whereas the Langmuir constant in L/mg is denoted by $K_L$, which is related to the adsorbate's affinity to the adsorbent (Wang and Guo, 2020a).

Another approach to express the Langmuir isotherm model is as follows (A.O, 2012): Eq. (7)

$$q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \tag{7}$$

### 4.1.2 Freundlich isotherm model

In 1906, Freundlich proposed an empirical equation to characterize the adsorbent surface's multilayer and non-uniform distribution of molecules at equilibrium (Gaballah et al., 1997). Additionally, it is a two-parameter isotherm that is frequently employed in wastewater treatment. It implies that stronger binding sites are occupied first, and that the intensity of adsorption reduces as the degree of occupation increases. Although this equation is frequently employed for its simplicity, it is thermodynamically insufficient because it violates Henry's law at low concentrations. Freundlich isotherm is shown in Eq.(8) (Repo, 2011):

$$log\, q_m = log\, K_F + \frac{1}{n} log\, C_e \tag{8}$$

Here, the number of molecules adsorbed to the adsorbent surface at any given moment is represented by $q_m$ in mg/g and the equilibrium, concentration is represented by $C_e$ in mg/L The Freundlich constant and exponent are denoted by the letters $K_F$ and n respectively. A number of 1/n less than 1 indicates that the adsorption process is chemical; a value greater than 1 indicates that the adsorption process is more physical; 1/n value closer to zero suggests greater heterogeneity of the surface. As n is more than unity, it shows that the molecules preferentially adsorb onto the surface i.e. adsorption is more intense.(Repo, 2011)

### 4.1.3 Sips isotherm model

The Sips isotherm is a merged form of the Langmuir and Freundlich models, which was developed for the purpose of forecasting adsorption in heterogeneous systems and overcoming the limitation imposed by the increasing concentration of the adsorbate related with the Freundlich isotherm. (Sips, 1948), This isotherm reduces to the Freundlich isotherm at low concentrations of the adsorbate and does not approach Henry's law; and predicts monolayer adsorption in a way similar to the Langmuir isotherm at high concentration of the adsorbate. Ebadi et al. created a three-parameter isotherm model that is the most suitable for monolayer adsorption on the adsorbent (Saadi et al., 2015). Figure 5 illustrates how one adsorbate molecule is adsorbed in a monolayer onto a $1/\beta_s$ adsorption site using the Sips model.
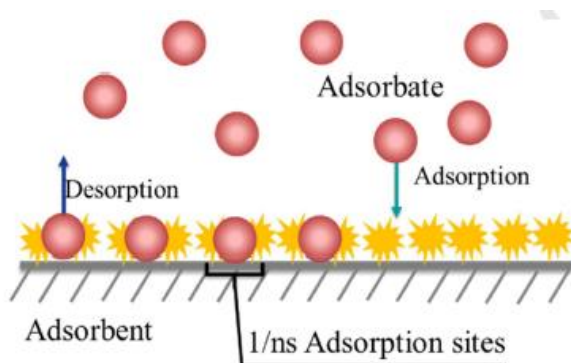


Figure 5. The adsorption mechanisms revealed by the Sips isotherm model (Wang and Guo, 2020a)

The expression of the Sips adsorption model is shown in Eq. (9) (GP and TP, 2012):

$$q_e = \frac{K_s C_e^{\beta_s}}{1 - a_s C_e^{\beta_s}} \tag{9}$$

where, Sips isotherm model constant is denoted by $K_s$ in L/g, Sips isotherm exponent is donated by $\beta_s$, and $a_s$ represent Sips isotherm model constant (L/g). The linearized form of the Sips model is presented in Eq. (10) (Elmorsi and Elmorsi, 2011):

$$\beta_s \ln C_e = -\ln\left(\frac{K_s}{q_e}\right) + \ln(a_s) \tag{10}$$

This model is well-suited for forecasting adsorption on heterogeneous surfaces, and it overcomes the Freundlich model's drawbacks, such as adsorbate concentration limitations (Travis and Etnier, 1981). In the Sips isotherm model, the parameters are concentration dependent (Elmorsi and Elmorsi, 2011; Chen, 2013), temperature and the isotherm constants alter when linearization and nonlinear regression are used to calculate them [50].

## 4.2       Adsorption kinetics

Adsorption kinetics is performed using a qt vs time curve that enables us to study the rate-controlling processes such as mass transfer and probable chemical reactions of a solute from an aqueous environment with the interface as well as determining the mechanism of adsorption at a particular adsorbents dose, temperature, flow rate, and pH (Blázquez et al., 2011). When it comes to the design of adsorption systems, it is critical to understand the adsorption kinetics. As illustrated in Figure 6, the kinetics of adsorption mass transfer consists of three stages. The outward diffusion is the initial step in the process. During this stage, the adsorbate is transmitted via the liquid film that surrounds the adsorbent. External diffusion is facilitated by the concentration difference between the bulk solution and the adsorbent's surface. The following phase is internal diffusion, which is related with adsorbate diffusion via the pore. The third phase begins with the adsorbate being trapped in the adsorbent's active regions. (Wang and Guo, 2020b)
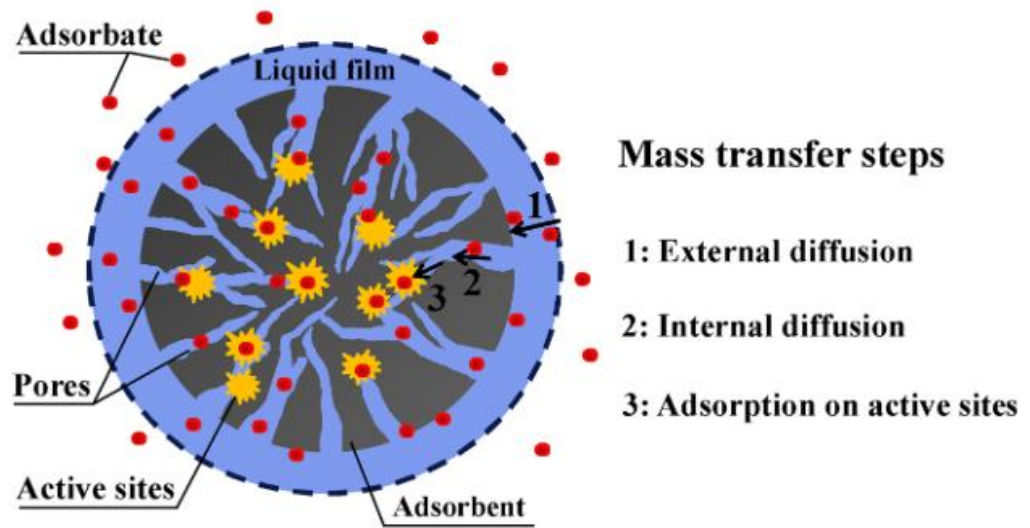
Figure 6. Adsorption mass transfer steps (Wang and Guo, 2020b)

Various adsorption kinetic models, such as the pseudo-first order (PFO) model, the pseudo-second-order (PSO) model, the mixed-order (MO) model, the Elovich model, have been developed to describe the adsorption kinetic process.

### 4.2.1 Pseudo-first-order model

Lagergren introduced the empirical kinetic equation in 1898 which is known as the pseudo-first-order kinetic model or Lagergren model and is extensively used for adsorption systems where the adsorption from the liquid phase has occurred. The model explains the relationship between the rate the sorption sites are occupied and the number of unoccupied sites. Therefore, the rate of adsorption increases with increasing adsorption sites. The differential form of the PFO model is described by Eq. (11) (Lagergren, S., no date)

$$\frac{dq}{dt} = k_1(q_e - q) \tag{11}$$

Integrating Eq. (11) leads to

$$\int_0^{q_t} \frac{1}{(q_e - q)} \, dq = \int_0^t k_1 \, dt \tag{12}$$

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \qquad (13)$$

Where, the adsorption capacity at equilibrium and at a time t (mins) are denoted by the variables $q_e$ (mg / g) and $q_t$ (mg / g), respectively, and $K_1$ denotes the first-order rate constant of adsorption ($min^{-1}$).

The linear plot of ln ($q_e - q_t$) against time was used to determine the rate constant $K_1$ (Hui et al., 2018). The PFO parameter $K_1$ is widely used to indicate the rate at which an adsorption equilibrium is reached (Plazinski, Rudzinski and Plazinska, 2009).

## 4.2.2 Pseudo-second-order model

It was initially employed to simulate the adsorption of lead adsorption onto peat by the PSO model Eq. (14) (Ho, Wase and Forster, 1996). Thereafter, when it came to describing adsorption processes, the PSO model gained widespread acceptance, and it continues to be used today. The PSO model was best fitted model used in the majority of research to forecast adsorption experimental data and to compute adsorption rate constants. The PSO model is based on the assumption that the solute's adsorption rate is proportional to the number of adsorbent's accessible sites. The amount of solute present on the adsorbent's surface influences the rate of reaction; the driving force ($q_e - q_t$) is relative to the quantity of active sites present on the surface of the adsorbent (X and B, 2005; HN et al., 2017; Tan and Hameed, 2017). The curvilinear form of PSO is depicted in Eq. (14)

$$\frac{dq_t}{dt} = K_2 (q_e - q_t)^2 \qquad (14)$$

The rate constant of the PSO is denoted by $K_2$. PSO is presented in the following linearized form, with the integral constraints for t (0, t) and qt (0, $q_t$) applied.

$$q_t = \frac{t}{\dfrac{1}{K_2 q_e{}^2} + \dfrac{t}{q_e}} \tag{15}$$

To determine the model parameters, it is always important to convert the nonlinear PSO form to the linear form Eq. (15)

$$\frac{t}{q_t} = \left[\frac{1}{K_2 q_e{}^2}\right] + \frac{t}{q_e} \tag{16}$$

With respect to the PSO linearized equations, Eq. (20) produces more accurate outcomes in comparison to the other linearized form. A graph of $\frac{t}{q_t}$ plotted against time may therefore be used to calculate the PSO constants straightforwardly.

### 4.2.3       Intraparticle diffusion model

Weber and Morris introduced the intraparticle diffusion model in 1962, and this model has been expanded to include the diffusion behaviour of liquids and solids in adsorbents. Intraparticle diffusion is used to identify the rate controlling stage during the adsorption process. The following equation (17) expresses the model of intra particle diffusion (Igwe, Mbonu and Abia, 2007).

$$q_t = k_{id}\, t^{0.5} + C \tag{17}$$

Where, $k_{id}$ denotes intra-particle diffusion constant (mg/gmin0.5) and C represents the boundary layer thickness. These parameters can be obtained by plotting qt vs $t^{0.5}$.

# 5        Adsorbent materials

Adsorption is one of the most successful techniques for eliminating a variety of micropollutants among the numerous treatment methods devised for water purification and WWT. Along with easy handling procedure and great efficiency, adsorption technology's significant advantages include the availability of a variety of adsorbents, as well as their affordability and cost-effectiveness (Nadaroglu, Kalkan and Demir, 2010) This chapter described the adsorbent use in this thesis.

## 5.1        Activated carbon

Carbon that has been treated to have a large number of microscopic, low-volume pores, which enhances the total surface area available for adsorption, is known as activated carbon (AC). The adsorption capacity of AC can be increased even more by further treatment. Numerous studies have found that the use of activated carbon in removing pharmaceuticals is effective, and that the material's great capacity for adsorption of pollutants makes it an excellent choice (Snyder et al., 2007; V, G and B, 2017). Activated carbon comes in several forms, but only two are intensively explored for their ability to adsorb pharmaceuticals: powdered activated carbon (PAC) and granular activated carbon (GAC). PAC is defined as fine granules with an average diameter of 0.15 to 0.25 mm and a particle size of less than 1 mm. GAC is distinguished from PAC mostly by its size. It contains bigger grain sizes, often ranging from 1.2 to 1.6 millimeters. GAC is also more expensive. The possible source of activated carbon is charcoal as well as naturally occurring materials with a high carbon concentration such as bamboo, wood, and coconut husk, among others. Activation of carbon compound requires physical or chemical treatment. Carbonization is a physical process that occurs when these materials are slowly heated to temperatures above 400°C in an oxygen-free environment, followed by treatment with typically steam or carbon dioxide, which acts as an oxidizing agent at elevated temperatures, producing submicroscopic spores and increasing surface area. One study indicated that cork powder waste may be used to make activated carbon by mixing the waste materials with $K_2CO_3$ (in a ratio of 1:1 by weight) and heating at 700°C for one hour. After that, the sample was allowed to cool before being rinsed

with distilled water until the pH reached 7, and then dried at 100°C. To complete the process, the sample was activated with steam at 750°C for one hour (Mestre et al., 2007).

Adsorption is how activated carbon removes pollutants from water in wastewater treatment plant. When activated carbon molecules are placed in water, they actively seek for other molecules to adsorb. Due to its high surface area and porous nature, activated carbon has a high capacity for chemical adsorption.

5.2        Hydrotalcite

Hydrotalcite, $Mg_6Al_2(OH)_{16}CO_3.nH_2O$ is made of a positively charged two-dimensional brucite-like layer and is used to neutralize the materials' anionic species. Numerous modifications have been undertaken in order to impart new properties to this material. The following properties have been developed: a. brucite layer's ability to exchange cations, b. interlayer anion exchange, c. tunable basicity of surface, and d. adsorption capacity. The hydrotalcite surface's concentration of OH and $HCO_3$ makes it a basic in nature. The following image depicts the hydrotalcite crystal structure.(Kaneda, 2007)
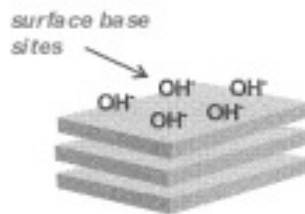


Figure 7. Hydrotalcite structure

Kuzawa et al. utilized hydrotalcite in adsorption studies, including phosphate removal and recovery from wastewater via the anionic action of the adsorbent, and obtained 47.3 mg/g adsorption capacity.(Kuzawa et al., 2005) Another study was conducted to remove diclofenac from wastewater and found that utilizing hydrotalcite as an addition to the adsorbent resulted in a 76.5 percent removal rate as well as reusability of the adsorbent.

Hydrotalcite's adsorption characteristics were found to be particularly advantageous for medicinal compounds.(Rosset et al., 2019)


5.3      Geopolymer


Geopolymers are generating significant interest these days due to their potential for using as a feasible and cost-effective substitute to inorganic cements in a variety of applications, including thermal insulating foams, military and aerospace (Giancaspro, Balaguru and Lyon, 2006), high-tech ceramics, protective coatings ('Geopolymer for Protective Coating of Transportation Infrastructures', 1998), fire-resistant building materials (Barbosa and MacKenzie, 2003),  refractory adhesives, wastewater treatment, and hybrid inorganic-organic composites (Zhang, Gong and Lu, 2004). These compounds aroused interest because of their outstanding thermal and chemical stability, long-term durability, as well as their excellent adhesive properties, and high mechanical strength. Furthermore, prior studies revealed that the production of geopolymers are inexpensive and can be produced from a wide variety of minerals and industrial by-products. This by-product may consist of naturally occurring aluminosilicate minerals (Xu and Van Deventer, 2000), fly ash (Rattanasak and Chindaprasirt, 2009), pozzolana (Verdolotti et al., 2008), Metakaolinite (Duxson et al., 2007), granulated blast furnace slag (Yunsheng et al., 2007), red mud and fly ash mixtures (Van Jaarsveld, Van Deventer and Lukey, 2002), red mud and Metakaolinite mixtures (Van Jaarsveld, Van Deventer and Lukey, 2002), and fly ash and Metakaolinite mixtures (Swanepoel and Strydom, 2002). Geopolymer has a composition that is comparable to that of zeolitic materials. However, the primary distinction between geopolymers and zeolite is that geopolymer materials have a three-dimensional silico-aluminate amorphous or semi amorphous microstructure (Davidovits, no date; Xu and Van Deventer, 2000) which is formed by linking $SiO_4$ and $AlO_4$ tetrahedra via the sharing of all the oxygen atoms, as defined by the empirical formula below:


$$M_n^+[-(SiO_2)_z - AlO_2 -]_n$$
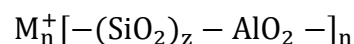
Where, M+ defines as an alkaline cation like $Na^+$, $K^+$, or $Ca^{2+}$ which is required for counteracting the negative charge of aluminum cation ($Al^{3+}$) in IV-fold coordination; z denotes the Si/Al ratio; and n denotes the degree of polymerization.

Davidovits suggested a number of geopolymer structural models based on the ratio of silicon to aluminum in the polymeric structure, named poly (sialate) (PS), poly (sialate-siloxo), and poly (sialate-disiloxo), as seen in Figure 8 (Davidovits, 1991)



Na-Poly(sialate)          (Na,K)-Poly(sialate-siloxo)          K-Poly(sialate-siloxo)
[Na-PS]                       [(Na,K)-PSS]                              [K-PSS]
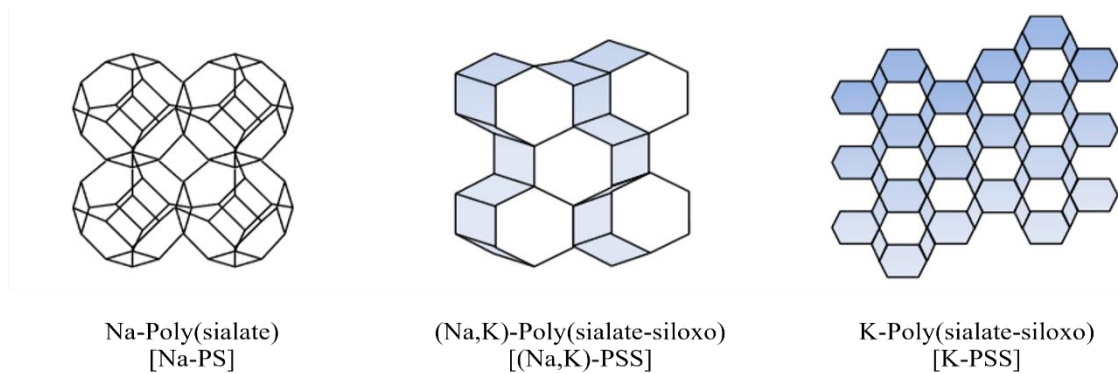
Figure 8. Structural models of geopolymers  (Davidovits, 1991)

Typically, the poly-condensation method is used to produce geopolymers, which result when a polymer precursor reacts with a metal hydroxide. The following two reactions depict the schematic synthesis of geopolymer material. (Xu and Van Deventer, 2000)

$$n(SiO_2Al_2O_2) + 2nSiO_2 + 4nH_2O + MOH \rightarrow M^+ + n(OH)_3 - Si - O - Al^- - O - Si - (OH)_3$$

Aluminosilicate
( raw material)

$$(HO)_2$$

Geopolymer precursor

$$n(OH)_3 - Si - O - Al^- - O - Si - (OH)_3 + MOH \rightarrow (M^+) - (-Si - O - Al^- - O - Si - O -) + 4nH_2O$$

$$(HO)_2$$

$$O \quad O \quad O$$

M=$Na^+, K^+$ or combination of them

Geopolymer

Figure 9. Synthesis reaction of geopolymer material

When it comes to removing harmful materials from industrial and residential effluents, using GEOs as adsorbents has emerged as a promising concept. Additionally, it has gained universal acceptability 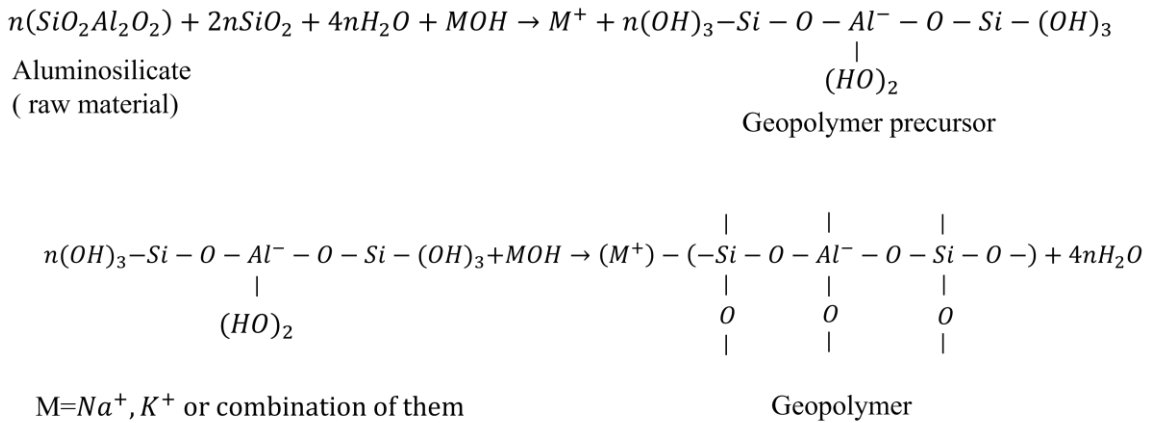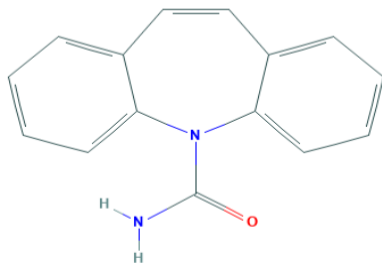for use in decolorizing water (Maleki et al., 2020). In recent investigations, it has been demonstrated that they are capable of serving as appropriate adsorbents for the removal of metals from aqueous solutions (Maleki et al., 2020). They have a highly linked and porous structure, have a high capacity for cation exchange, and have an affinity for metals, which enhances their ability to bind with cationic substances (Lertcumfu et al., 2020a). Numerous countries (KP et al., 2011) are currently exploring with their use as a substitute for Portland cements. Numerous studies have recently revealed that adsorbents derived from fly ash (FA) are extremely effective at removing methylene blue dye as well as metals such as $Cu^{2+}$, $Cd^{2+}$, $Cr^{3+}$, and $Pb^{2+}$ (T et al., 2015). Only a few articles have been published on the topic of using modified geomaterials to remove pharmaceuticals from aqueous environments. Salem Attia et al. utilized zeolite coated with magnetic nanoparticles as an adsorbent for pharmaceuticals and personal care products removal from water. (Salem Attia, Hu and Yin, 2013) Another study was done to remove metronidazole antibiotics from wastewater using clay modified with MnO nanoparticles.

As described above, geopolymer is a significant adsorbent and its efficiency to remove pharmaceutical compounds from the wastewater should be further explored.

# 6      Carbamazepine (CBZ)

CBZ is a tricyclic anticonvulsant and analgesic medication that is prescribed to treat epilepsy and chronic pain. The FDA approved carbamazepine for use in epilepsy in 1968, and it is still widely prescribed, with over 2 million prescriptions today, given annually in the U. S. alone. Due to its strong persistency, it is one of the medicines that is often identified in surface waters with concentrations more than tenfold to those of other micropollutants (S et al., 2011). The various properties of CBZ are shown in Table 1.

Table 1. CBZ's physicochemical properties

| Chemical structure |  |
|---|---|
| Molecular formula | $C_{15} - H_{12} - N_2 - O$ |
| Molecular weight | 236.27 |
| pKa | 2.3 |
| logKow | 2.45 |
| Distribution coefficient, $K_d$ (L/g) | 1.2 |

Numerous studies conducted on pharmaceuticals removal from WWs shows that traditional treatment techniques are ineffective in removing these chemicals from wastewater streams (V et al., 2015). Coagulation-flocculation, chemical oxidation, and adsorption can all be used to remove micropollutants from effluents. When the distribution coefficient of micropollutants is low, it is hard to eradicate them from the body using traditional treatment methods. Due to carbamazepine's low distribution coefficient (Kd=1.2 L g -1), it cannot be removed via anaerobic digestion. As a result of effluents from urban wastewater treatment plants being released into the environment, CBZ can be discovered in aquatic habitats and subsequently in drinking water. Developing an effective post-treatment strategy may assist in limiting carbamazepine discharge into the surface waters.

# 7 Additive manufacturing technology

Using 3D models to fabricate parts layer-by-layer, additive manufacturing (AM) techniques have the ability to revolutionize and, in some cases, totally modify existing traditional manufacturing techniques. Contrary to traditional manufacturing, which often includes milling or other techniques to eliminate extra material, it constructs product layer by layer with exact geometric designs using CAD or 3D scanners. For prototyping and the fabrication of geometrically complex elements, it is especially effective. It was originally developed already in the 1980s, but due to its complexity and cost, it had little applications. However, after the year 2000, the technology has become very easy and economical, making it ideal for a broad variety of applications such as tool and component production and product design as well as electronics goods and metalworking, plastics processing, dentistry, medical applications, aerospace engineering, and wastewater treatment. AM can be categorized into the seven process categories or types listed below depending on the techniques employed to build layers, as defined by ISO/ASTM standards ('The National Standards Authority of Ireland (NSAI) produces the following categories of formal documents', no date). The Additive manufacturing technology is classified as follows according to the working principle:

- Vat photopolymerization

- Material Jetting (MJ)

- Binder Jetting

- Powder bed fusion (PBF)

- Direct energy deposition (DED)

- Sheet lamination

- Material extrusion

Material jetting additive manufacturing technology was used to manufacture 3D adsorbents. The basic principle of this process is explained below:
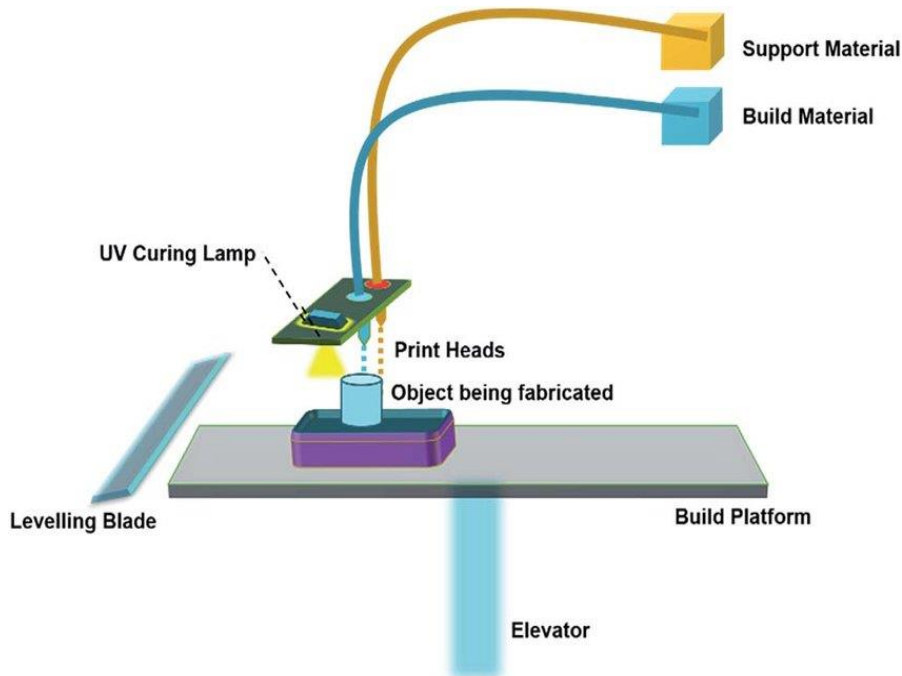


Figure 10. Schematic illustration of the Material jetting method (Sireesha et al., 2018)

Material jetting is a process in which, build material droplets are carefully positioned layer by layer into the build platform to create a predetermined 3D structure. MJ Printing is an inkjet printing technology that employs piezoelectric technology to droplets the material onto a build surface layer after layer, similar to how a printer prints on a sheet of paper. The print head deposits material droplets onto the build platform during this operation, which are later consolidated to form the first layer. On top of the existing layers, New layers are put to produce a three-dimensional shape. UV radiation is then used to cure or harden the multiple layers of material. MJ is depicted schematically in Figure 10. This category of printing technologies cover the following frequently employed printing technologies: Continuous Inkjet Printing (CIJ), Drop on Demand (DOD), Nanoparticle jetting. MJ is the sole additive manufacturing process capable of achieving the maximum Z-direction resolution  while maintaining the layer thicknesses as low as 16mm among all other AM technologies. Generally CIJ and DOD produce 3D printing models using materials such as polyamide, ABS, PLA, and their composites (H. Sirringhaus and T. Shimoda, 2011).

# 8       Materials and methods

## 8.1       Materials and chemicals

AC, hydrotalcite and geopolymer materials were used as adsorbents in this research. Powdered forms of those materials were also used to produce 3D printed adsorbents using a direct ink writing-based 3D printer. The powdered form of carbamazepine (CBZ, purity 98.0 percent) was used to make the sample for adsorption treatment. Sodium hydroxide and hydrochloric acid were used to adjust the pH of the solution. All compounds were brought from Sigma Aldrich. All compounds were applied without additional purification, and all experiments utilized ultra-pure deionized (DI) water as the aqueous matrix.

## 8.2       Methods

Adsorbent fabrication procedure: The 3D printed geopolymer was prepared by direct ink writing, DIW additive manufacturing process by collaborators from University of Padova, Italy. For formulating ink in DIW, metakaolin (alumino-silicate building blocks), sodium silicate solution, sodium hydroxide and distilled water was used. The molar ratio of $Na_2O/SiO_2 = 0.263$; $SiO_2/Al_2O_3 = 3.8$; $Na_2O/Al_2O_3 = 1$ were maintained, and the ratio of sodium hydroxide and water was required to be adjusted to full fill the rheological requirements as it is the key factor for the DIW process. To enhance the pseudoplasticity of the ink, 2.0 dwt.% sodium bentonite (inks containing activated carbon) and 4.4 dwt.% sodium bentonite (inks containing hydrotalcite) (Clear OFF Minerals, UK) was added to perform as a rheological agent into the alkaline solution and stirred thoroughly until a homogeneous mixture was obtained. After that, 26.8 dwt.% of activated carbon and 25.2 dwt.% of hydrotalcite were added to inks respectively. And lastly to retard the geo-polymerization process, metakaolin was added and agitated for ten minutes in a cold-water bath.
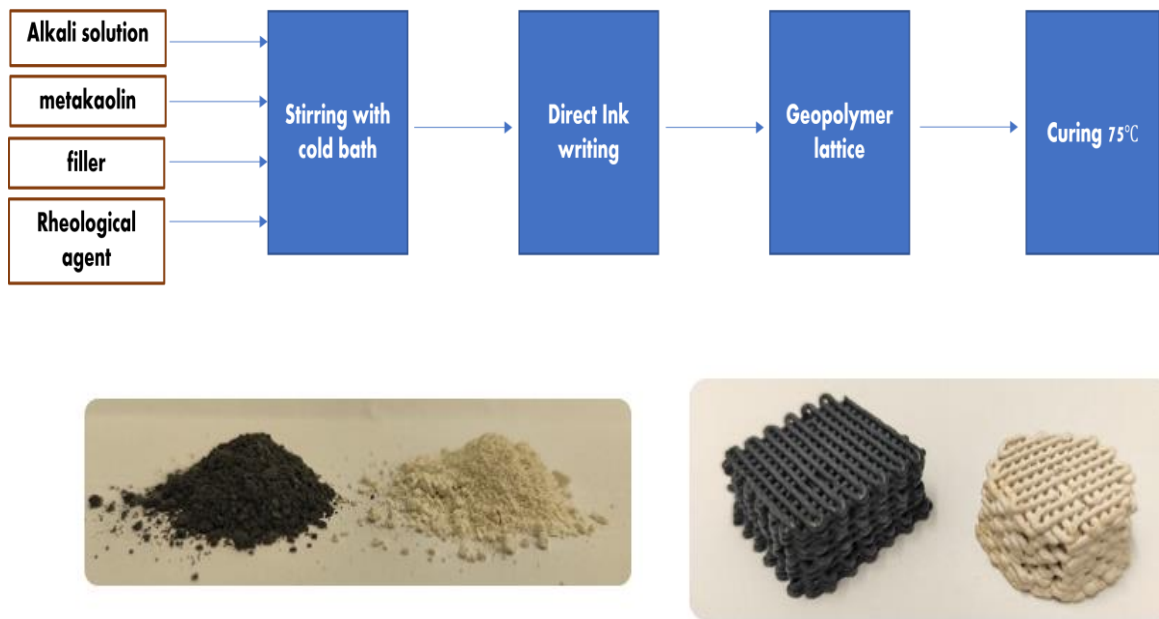
Figure 11. Manufacturing process for geopolymer lattices.

According to the different types of materials and fabrication techniques, the varied percentages of filler are determined by the highest permissible amount that can be introduced in order to achieve a homogeneous mixture with the ideal viscosity for extrusion or dripping. Once it had been well blended, it was then placed into a syringe and mounted with an 840 μm (Nordson Italia S.p.a., Segrate, Italy) conical nozzles of Delta printed DIW system (Delta Wasp 2040 Turbo, Wasproject, Massa Lombarda, Italy) containing a pressure vessel as well as a mechanism for extruding screw paste. The printed 3D structure in a lattice form was kept in air to avoid curing and clogging problems. The obtained materials have the following properties- 50% porosity, 0.8 mm spanning distance among filaments, dimensionality (20mm width and 9.6mm height). Following printing, the samples were heated in a muffle furnace in a confined system for two days at 75 °C to finish the geopolymerization reaction. The powder geopolymer utilized in the adsorption studies was created by injecting the same ink into a confined mold, heating it at 75°C for two days, and then pulverizing it. The fabrication methods of Geopolymer lattices with activated carbon and hydrotalcite is depicted in Figure 11

**Carbamazepine solution preparation:** Carbamazepine was utilized for preparing simulated wastewater. The solubility of carbamazepine in water 125.9 mg/L at room

temperature has been reported (Borisover, Sela and Chefetz, 2011). However, few research reported a different solubility value such as US EPA reported solubility in water of 18 mg/L. In 2000 mL of DI water, 0.2000 g of CBZ power was thoroughly dissolved with using a magnetic stirrer for 24hr at 55℃, yielding a stock solution of CBZ (100ppm). Hydrochloric acid (≥37%) and sodium hydroxide were also obtained from Sigma Aldrich and were used for preparation 1M and 0.1M solutions for pH adjustment.

**Adsorption experiments:** Adsorption tests were done in a batch mode at 25°C. CBZ concentrations were determined before to and following adsorption through high-performance liquid chromatography analysis. Batch adsorption samples were produced by diluting carbamazepine to a concentration of 10ppm from a stock solution of 100ppm. In general, 10 mL of stock solution containing 10 ppm carbamazepine was put in 10 mL plastic tubes containing 10 mg milled composite of AC and geopolymer or milled composite of hydrotalcite and geopolymer adsorbent or 3D printed AC or hydrotalcite additively manufactured geopolymer adsorbent as a ratio of 1:1. According to the experiment requirements, an orbital shaker set at 300 rpm was used to shake the mixture for a predetermined duration of time at 25°C. The solution was filtered once adsorption was complete using plastic syringe filters (Phenex RC 0.20 μm) and the filtrate was tested using HPLC. Equations (18) and (19) were used to compute the quantity of carbamazepine removed from the synthetic solution by adsorption capacity or recovery %.

$$Removal(\%) = \frac{C_i - C_e}{C_i} \times 100\%$$

(18)

where $C_i$ and $C_e$ denote the analyte concentrations in mg/L prior to and following carbamazepine adsorption, respectively.

$$q_e = \frac{(C_i - C_e)}{m} \times V$$

(19)

Where, the equilibrium adsorption capacity in mg/g is represented by $q_e$, dry weight of adsorbent in g is denoted by m, and the volume of a sample in mL is denoted by V.

**pH dependency test:** To determine the effect of pH on carbamazepine elimination, 50 mL plastic disposable tubes with a total capacity of 10 mL were employed with twelve different pH values (1 to 12). At 25℃, the carbamazepine concentration was 10 ppm, and the adsorbent dosage was 0.001 g/mL. After pH correction, samples were agitated at 300 rpm using a mechanical shaker. The adsorbent was in contact with the pharmaceutical for 24 hours.

**Adsorption isotherm:** Carbamazepine adsorption was performed using a range of starting concentrations (1-100 ppm) and a fixed adsorbent dosage (0.001 g/ml) in 50 mL plastic disposable tubes. For 24 hours, the suspensions were shaken at 300 rpm at 25℃. The solution pH was maintained at 9.0 for powdered and 3D printed AC additively manufactured geopolymer adsorbents and at pH 1 for powdered geopolymer, since this pH provided the highest adsorbent capacity. Additionally, the pH of the 3D printed hydrotalcite additively manufactured geopolymer was kept pH above 2.5 because the 3D lattice structure dissolved below that pH range, even if the geopolymer's adsorption ability decreased with rising pH value.

**Kinetic studies:** Effect of contact time on CBZ elimination by adsorbent was investigated at initial concentrations 50 ppm with a fixed adsorbent dosage (0.001 g/mL) with pH value used in isotherm experimental section. The samples were agitated using an orbital shaker at a time range of 5 min, 15 min, 30 min, 60 min, 120 min, 240 min, 480 min, 720 min, and 1440 min. The suspension was vigorously agitated by magnetic stirrer and the evenly dispersed adsorbent granules and solution were extracted simultaneously in each predetermined time intervals. The preceding step's filtration and storage process followed for preparing samples for further analysis.

8.3        Adsorbent characterization

**HPLC analysis:** HPLC with a diode array detector (Agilent 1260 series) was used to determine the medicinal residues. Chromatographic separation was carried out at room

temperature using the reverse stationary phase Eclipse XDB-C18 (150 x 4.6, particle size 5m). The flow rate was 0.2 mL/min, and the injection volume were 10 l. A – 0.1 formic acid and B – acetonitrile was used as mobile phases. Gradient elution was used in the following manner: For 3 minutes, 20% of B was administered; for 25 minutes, 45 percent of B was applied; for 27 minutes, 30% of B was applied; and for 30 minutes, starting conditions were applied. The detected medication (CBZ) had a maximum absorbance of 290 nm.

**Fourier transform infrared spectroscopy (FTIR):** FTIR coupled with a universal ATR module was employed to identify the adsorbent's surface functional groups. For each FTIR sample run with a 1 $cm^{-1}$ data interval, the 4000-400 $cm^{-1}$ range wave number with triple absorbance mode was used. Finally, all recorded spectra were corrected with baseline and ART.

# 9 Result and discussion

This chapter covers the characterisation of the adsorbent and the analysis of the carbamazepine adsorption process by determining the optimal pH level, adsorption isotherm, and kinetics.

## 9.1 FTIR analysis

The Fourier transform infrared (FTIR) analysis was performed to examine the surface functionality of activated carbon and geopolymer materials. Adsorption capacity of adsorbent materials is determined by the porosity and chemical reactivity of the functional groups present on the surface of the substance. The Figure 12 (a) depicts the Fourier transform infrared (FTIR) spectra of powdered geopolymer and hydrotalcite mixture and activated carbon and geopolymer mixture.

The following peaks are visible in the FTIR spectrum of Hydrotalcite mixed geopolymer: 3342 cm-1 is assigned to the O-H stretching vibration, 2920 cm-1 is assigned to the bond associated $CO_2$ and water, 1655 cm-1 is assigned to the O-H bond bending vibration, 1376 cm-1 is assigned to the $CO_3^{2-}$ anion interlayer, confirming the presence of hydrotalcite compound, as the significant peak arise for hydrotalcite in following ranges: 3500-3470 cm-1, 2364-2923 cm-1 and 1500-1300 cm-1(Mališová et al., 2018) while 991 cm-1 is assigned to the Si-O-Al symmetric vibration, and 451 cm-1 is assigned to the C=C bond, all of which are significant peaks for geopolymer identification (Khan et al., 2014). Due to the presence of water and the silanol group, the OH asymmetric stretching peak can be seen among them. According to Catherine et al., the 991 cm-1 peak confirms the geopolymer structure by indicating the presence of a Si-O-Al bond.(Catherine A. Rees et al., 2007)

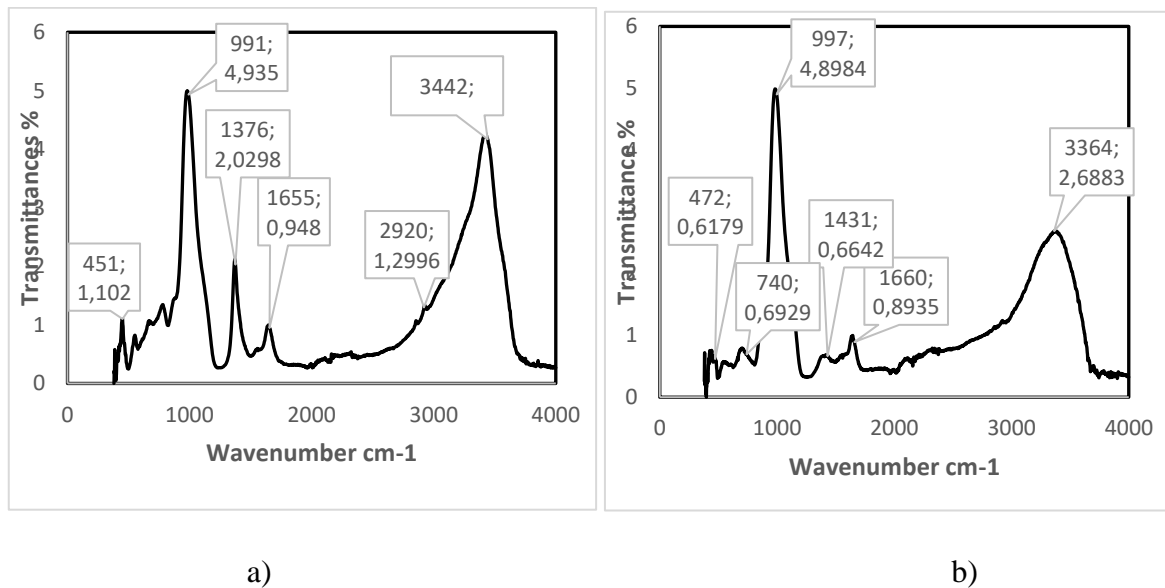a)                                                          b)

Figure 12. FTIR spectrum of a) hydrotalcite mixed geopolymer powder and b) activated carbon mixed geopolymer powder

Activated carbon has the following surface functional groups: hydroxyl groups, carboxyl groups, and carbonyl groups, as shown in Figure 12(b) by the FTIR spectra after each peak. The signal at 3364 cm-1 corresponds to the O-H functional group, whereas 1660 cm-1 corresponds to the existence of C-O and C=O groups, and 1431 cm-1 confirms the OH bond in the carboxylic acid group. (Şencan and Kiliç, 2015) Another wide peak appears at 997 cm-1 assign to symmetric vibration of Si-O-Al bond, and 472 cm-1 assign C=C that confirm the presence of geopolymer in the samples.

## 9.2        pH dependency test

pH is a critical parameter in the adsorption process because it affects the adsorbent's surface functionality through protonation and deprotonation of the adsorbent's functional groups. As a result, the optimal pH values must be established prior to studying the adsorption process in detail for pollutant removal. The pH values and related adsorption capacities of CBZ adsorption on the milled composite of activated carbon and geopolymer are shown in Figure 13.
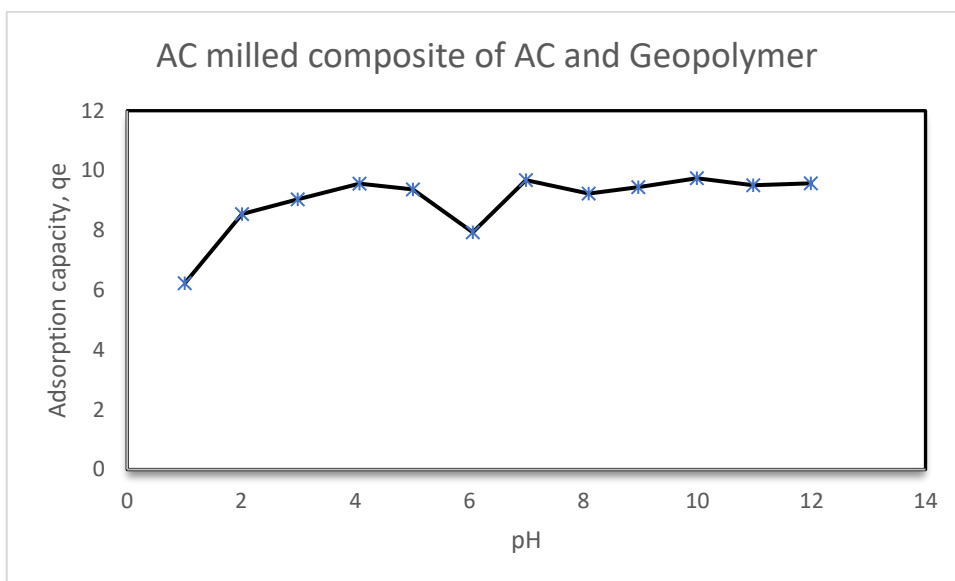
Figure 13. pH effect on carbamazepine removal by milled composite of activated carbon and geopolymer.

It is apparent to see that the adsorption capacity increases with rising pH and then decreases with increasing pH value removal. After doing the first set of experiments with various pH values, it was determined that pH 9 provided the optimal value for maximal CBZ elimination. Comparable results have been obtained earlier by Bežanović et al. (Bežanović et al., no date).

Similarly, experiments were performed using hydrotalcite mixed geopolymer powder to determine the optimum pH for CBZ removal, despite the fact that CBZ removal is very low through hydrotalcite mixed geopolymer adsorption. The adsorption capacity was found to be much greater at pH 1; however, when pH increased slightly, the adsorption capacity decreased dramatically, and after pH 2, the adsorption capacity remained almost constant up to pH 12. A little increase in removal was seen at pH 8, as shown in Figure 14.
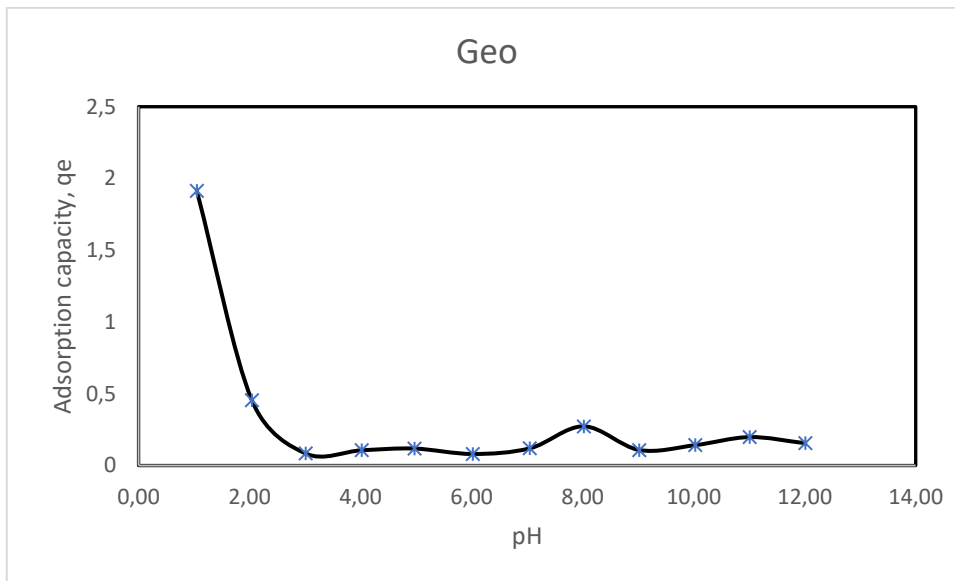
Figure 14. pH effect on carbamazepine removal by hydrotalcite mixed geopolymer powder.

9.3        Isotherm study

The isotherm study was performed to establish a relationship between the equilibrium concentration and the concentration of adsorbate on the adsorbent. Several previous models, including as Langmuir, Freundlich, sips, and Redlich Peterson, were developed for determining the correlation between adsorbate in the solution and bound by the adsorbent under equilibrium conditions. The non-linear model equation and the ERRSQ Error function were used to fit the data. The picture shows experimental data and non-linear model isotherm fit for an adsorbent based on milled composite of activated carbon and geopolymer.

According to Figure 15, the Langmuir isotherm model was selected as a more relevant model for experimental data compared to Freundlich model, despite the fact that the $R^2$ (0.5309) value was insufficient. The model predicted the maximal adsorption capacity $q_m$ of 30.94 mg/g, which was close to experimental data, and the Langmuir constant, KL 1.71 L/mg. This constant is proportional to the energy directed toward adsorption. The RL constant is calculated using the KL value and the starting concentration $C_i$. The RL value denotes the kind of adsorption in the following manner: RL>1 indicates an unfavourable condition,

RL=1 indicates a linear condition, and 0<RL>1 indicates a favourable condition. RL=0 is an irreversible condition.(Cai, Zheng and Fang, 2015) In contrast, the Freundlich model fits gave $R^2$ value as low as 0.0582 with K value of 29.2703 mg/g, indicating adsorption capacity, and 1/n value of 0.32255, indicating the energy distribution and heterogeneity of the adsorbent. The preferred value of n is greater than 1, and a greater n number indicates a greater adsorption capability (Repo, 2011). However, as Freundlich model fit was very poor, these parameter values are not reliable.
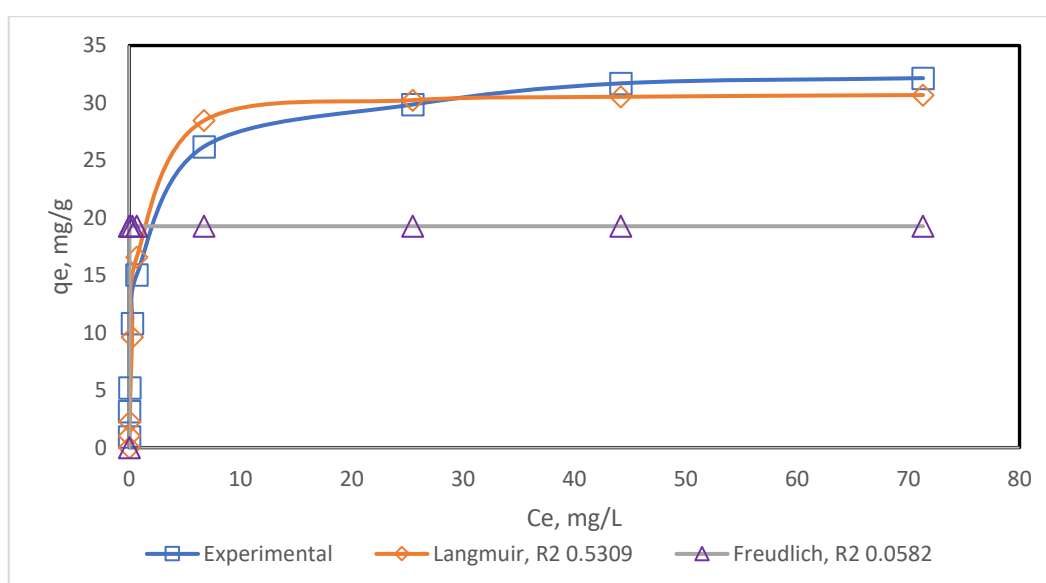


Figure 15. Isotherm curve of the milled composite of activated carbon and geopolymer (1 ppm, 3 ppm, 5 ppm, 10 ppm, 20 ppm, 30 ppm, 50 ppm, 70 ppm) at 9 pH using experimental data to fit Langmuir and Freudlich non-linear model.

The Figure 16 depicts the experimental results plotted against several model assumptions for a 3D printed geopolymer fabricated adsorbent. The Sips model was chosen as the best appropriate model for the adsorption process due to its R2 value of 0.9507, indicating improved model predictability. The model predicts the maximum adsorption capacity qm 5.5931 mg/g, the affinity constant Ks 0.1465 and the model's exponent Bs 0.0215.(GP and TP, 2012) Following the Sips model, Langmuir model was used to get an $R^2$ value of 0.9406 with a maximum adsorption capacity of $q_m$ 5.593 mg/g and KL 0.0239. Following that, the Redlich Peterson model with an $R^2$ value of 0.8759 provides unit values for A and B. (GP

and TP, 2012) Freundlich model does not demonstrate adequate model fitting, as shown by the R2 value of 0.1793. (Repo, 2011)
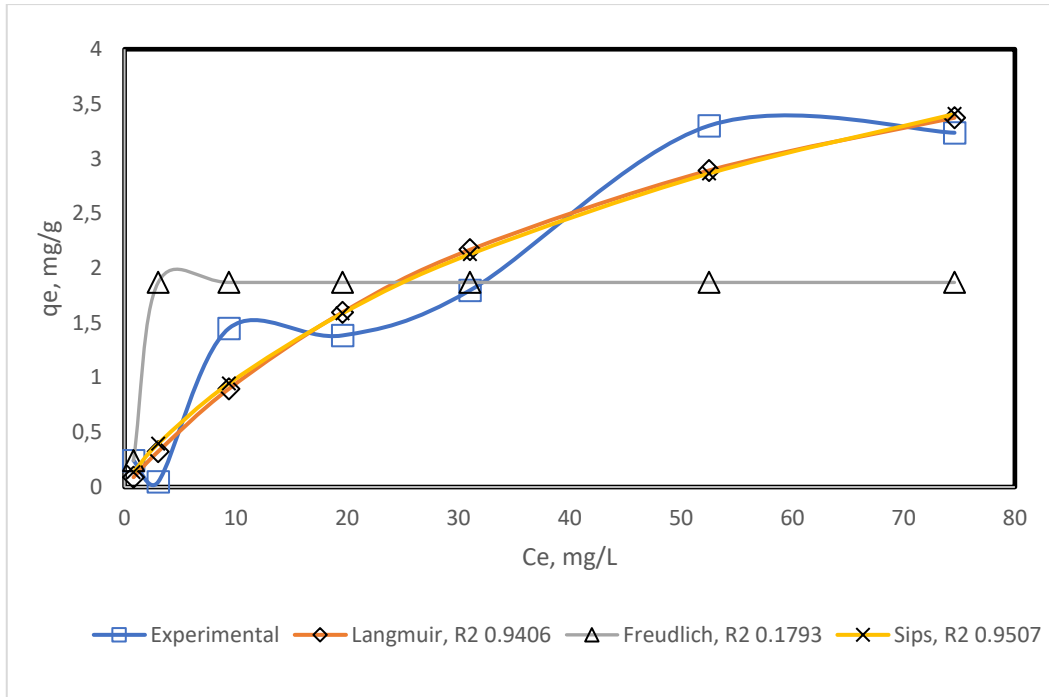


Figure 16. Isotherm curve of 3D printed geopolymer with hydrotalcite additive (1 ppm, 3 ppm, 5 ppm, 10 ppm, 20 ppm, 30 ppm, 50 ppm, 70 ppm) at 2.5 pH using experimental data to fit Langmuir, Freudlich, and Sips non-linear model,

9.4        Adsorption Kinetic study

The adsorption kinetics were investigated in order to determine the impact of contact time on the adsorption process. Four distinct equilibrium times were found for four different kinds of adsorbents (milled composite of activated carbon and geopolymer, activated carbon fabricated 3D printed geopolymer, milled composite of geopolymer and hydrotalcite, and hydrotalcite fabricated 3D printed geopolymer).

Figure 17. Kinetic model a. hydrotalcite fabricated 3d geopolymer, b. mixture of powdered geopolymer and hydrotalcite, c. Activated carbon fabricated 3d geopolymer and d. milled composite of activated carbon and geopolymer.

As can be seen from Figure 17, all adsorption processes followed the intraparticle diffusion model reaction kinetics with an $R^2$ value more than 0.9, indicating a more accurate model prediction and a high degree of correlation with the experim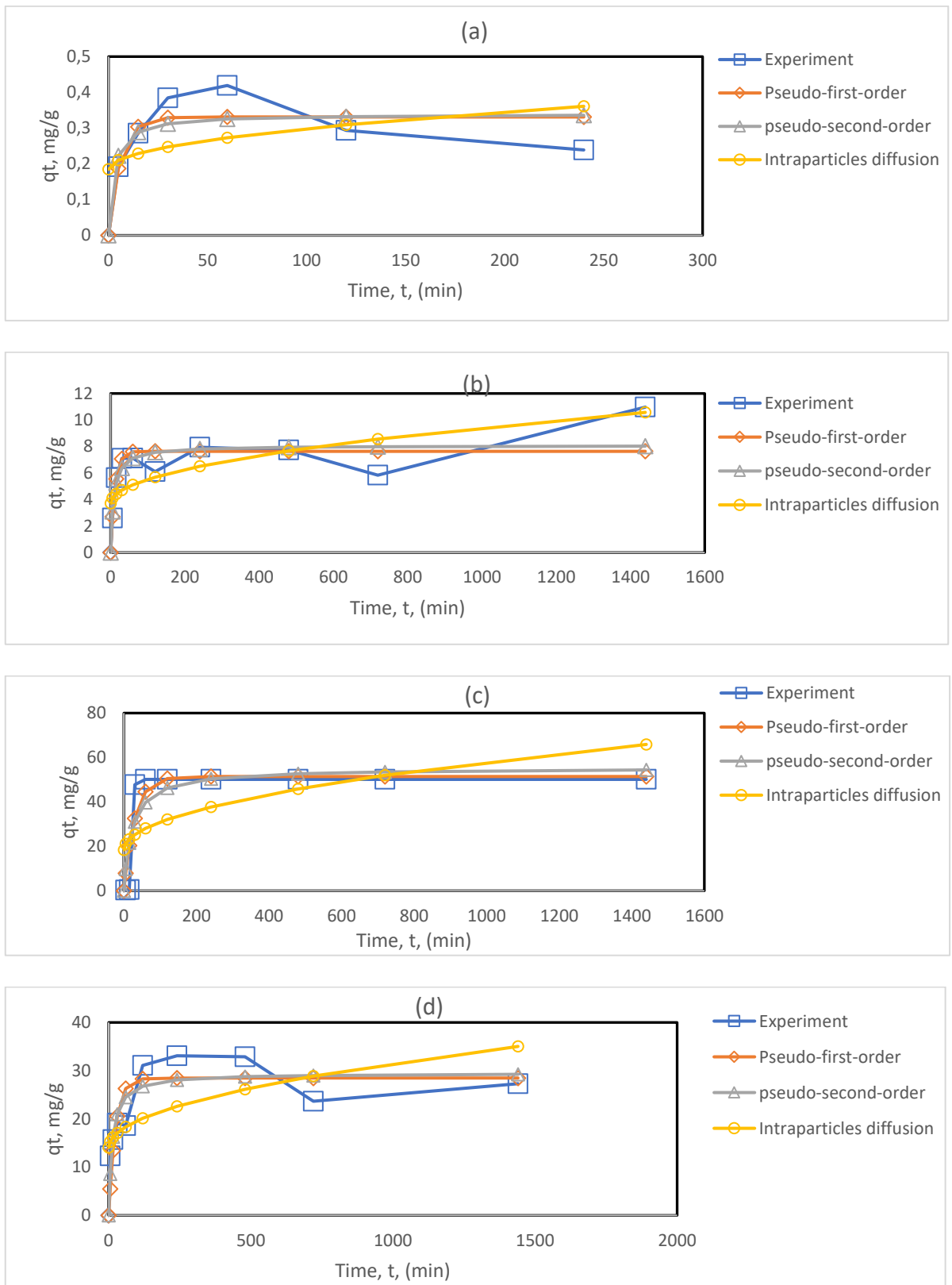ental data. Additionally, pseudo first and pseudo second order models were applied to the experimental data, however their prediction was not significant due to their low $R^2$ values. All models were fitted using a nonlinear model equation. (Plazinski, Rudzinski and Plazinska, 2009) (Ho, Wase and Forster, 1996).

Three distinct model parameter values, as well as the $R^2$ values, are summarized in Table 2

Table 2. Summary of kinetic modeling results

| Adsorbent | Model | Constant | | R2 |
|---|---|---|---|---|
| Hydrotalcite fabricated 3D printed geopolymer | Pseudo first order | k1 | 0,166475089 | 0,2495 |
| | | qe | 0,331116481 | |
| | Pseudo second order | k2 | 1,119319594 | 0,2 |
| | | qe | 0,339598462 | |
| | Intraparticle diffusion | Kid | 0,166475089 | 0,2495 |
| | | C | 0,331116481 | |
| Milled composite of hydrotalcite and geopolymer powder | Pseudo first order | k1 | 0,086766305 | 0,1763 |
| | | qe | 7,637307609 | |
| | Pseudo second order | k2 | 0,01545902 | 0,2534 |
| | | qe | 8,072404585 | |
| | Intraparticle diffusion | Kid | 0,180811239 | 0.9175 |
| | | C | 3,711779424 | |
| Activated carbon fabricated 3D printed geopolymer | Pseudo first order | k1 | 0,033440989 | 0.3027 |
| | | qe | 51,45854944 | |
| | Pseudo second order | k2 | 0,000775494 | 0.3987 |
| | | qe | 55,29151049 | |
| | Intraparticle diffusion | Kid | 1,25239563 | 0.9175 |
| | | C | 18,36763789 | |
| Milled composite of activated carbon and geopolymer | Pseudo first order | k1 | 0,042687873 | 0,2658 |
| | | qe | 28,48411025 | |
| | Pseudo second order | k2 | 0,002791 | 0,306 |
| | | qe | 29,49718903 | |
| | Intraparticle diffusion | Kid | 0,552681629 | 0.9175 |
| | | C | 14,05801882 | |
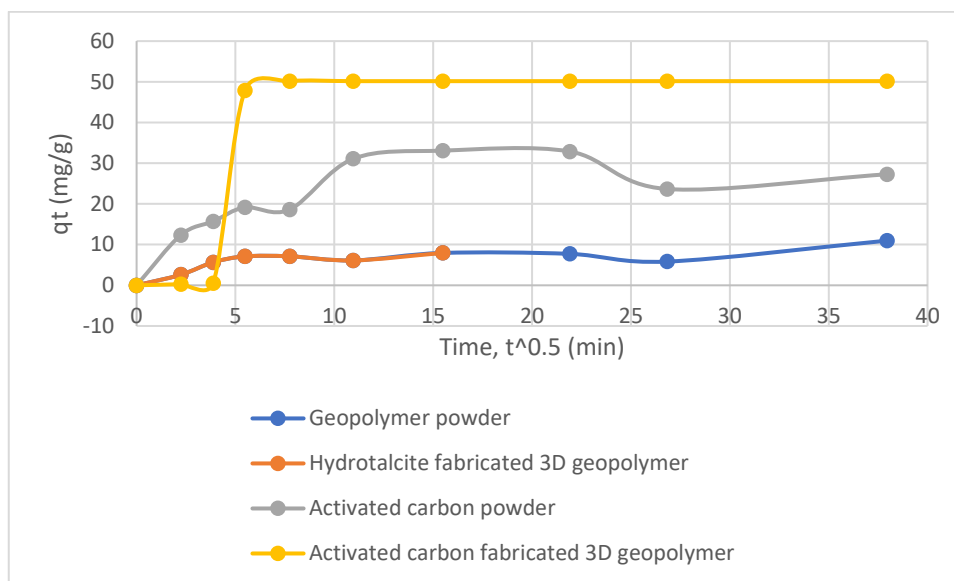
Figure 18. Intraparticle kinetic model

The rate limiting step in the intraparticle adsorption model was identified by plotting qt vs t0.5 and comparing it to the multilinear adsorption profile presented in Figure 18. Based on this model adsorption occurs in three stages during the adsorption process. The first step line denotes the beginning phase; the second step continues with surface diffusion and pose diffusion of adsorbed particles via the adsorbent surface; and during the third step adsorbent becomes saturated with particles absorption from solution and provides a plateau curve. The concept for the mechanism was derived from the following source:(Igwe, Mbonu and Abia, 2007)

## 9.5        Adsorption mechanism

This section will discuss the mechanism of CBZ adsorption. To comprehend the adsorption process, one must first comprehend the adsorbate and adsorbent functionalities. The Figure 19 depicts a speciation diagram of CBZ using pure water with varying pH values. The dissociation of CBZ is typically determined using the Henderson-Hasselbalch equation, which demonstrates that between pH values of 3 and 11, the CBZ molecule acts as neutral. (BIZI, 2019)
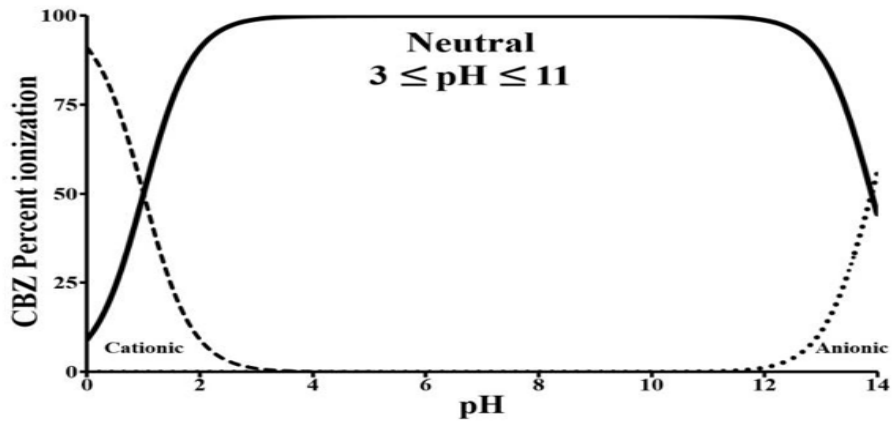
Figure 19. Speciation diagram of CBZ as function of pH determined based on pKa1=1 and pKa2=13 (Source: (BIZI, 2019))

Since the CBZ molecule is a neutral chemical with a pH range of 3 to 11, adsorption between activated carbon and CBZ occurs via hydrogen bonding.
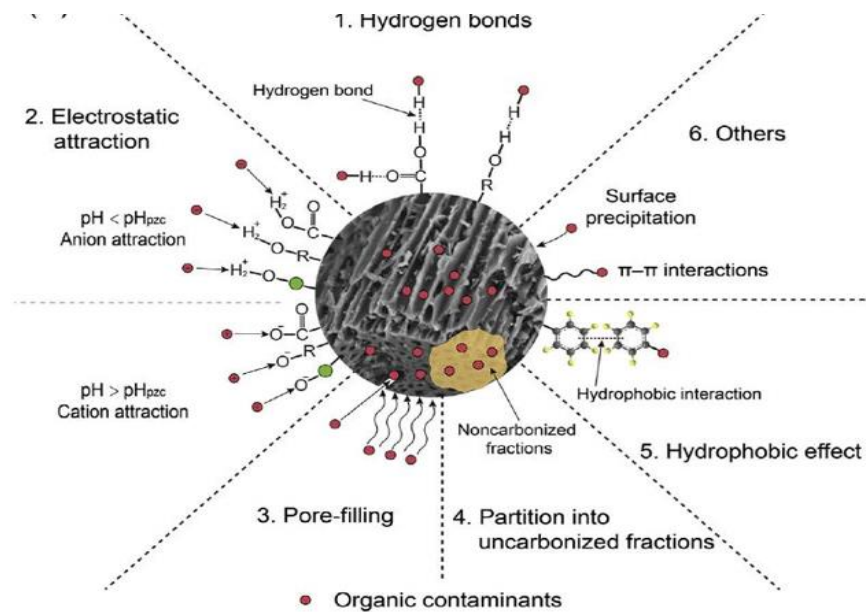


Figure 20. Adsorption mechanism summary for organic contaminants (Tan et al., 2014)

At low pH, CZP adsorption is slightly decreased because the surface of the AC-geopolymer becomes positive owing to protonation and a portion of CZP is in cationic form. Electrostatic

repulsion acts as a barrier to adsorption in this situation. As a result of this finding, it is evident that HT-geopolymers lack active sites for CPZ adsorption.

9.6        Adsorbent efficiency comparison

The following Table 3 shows the maximum adsorption capacity of each adsorbent material under optimal conditions with others works. According to the table, milled composite of activated carbon and geopolymer is a promising adsorbent material for CBZ elimination. When milled composite of activated carbon and geopolymer materials were utilized to form a 3D printed adsorbent, the removal efficiency was increased by thrice. On the other hand, the use of milled composite of hydrotalcite and geopolymer to remove CBZ from water demonstrated negligible removal effectiveness; the highest efficiency was around 10 mg/g, also showing that fabricated geopolymer possessed a reduced adsorptive ability. The explanation for this consequence is that whereas milled composite of geopolymer powder demonstrated adsorption characteristics in extremely acidic conditions, 3D lattice adsorbents were not stable in extremely acidic conditions. To address this disadvantage, adsorption experiments on 3D printed adsorbents were done at pH 2.5, whereas for milled composite of hydrotalcite and geopolymer adsorbents tests were conducted at pH 1 and due to this reason adsorption efficiency decreased. Moreover, beyond pH 1, adsorption effectiveness decreased with decreasing pH and was shown to be plateau after pH 2 with adsorption capacity around 1 mg/g.

Table 3 Adsorbent comparison table

| Name of the adsorbent | Operating pH | Duration (h) | Adsorbent capacity (mg/g) | Ref. |
|---|---|---|---|---|
| Graphene oxide nanoplates | 2 | 2 | 9.2 | (Bhattacharya et al., 2020) |
| Molecular imprinted polymer | | | 28.40 | (He et al., 2020) |
| Super activated carbon | 6-8.5 | | 235 | (BIZI, 2019) |
| Hydrotalcite mixed geopolymer | 1 | 24 | 10.97 | This work |

| | | | | |
|---|---|---|---|---|
| 3D printed geopolymer with Hydrotalcite additive | 2.5 | 24 | 3.30 | This work |
| Activated carbon mixed geopolymer | 9 | 6 | 33.04 | This work |
| 3D printed geopolymer with Activated carbon additive | 9 | 12 | 100.97 | This work |

Based on this study the usage of 3D printed adsorbents was found to be advantageous especially in the case of 3D-printed activated carbon structures. Possible disadvantages found were related to the stability of the 3D-strucures. Hydrotalcite as an additive did not improve the adsorption capacity of geopolymer.

# 10 Conclusions and future studies

The purpose of this thesis was to perform research on the removal of carbamazepine from wastewater utilizing four distinct adsorbent types (milled composite of activated carbon and geopolymer, milled composite of hydrotalcite and geopolymer, and 3D printed geopolymer with hydrotalcite and activated carbon additive). The batch adsorption research was conducted to determine the removal effectiveness, as well as to determine the optimal conditions such as adsorbent dosage, pH, and temperature, as well as to examine the isotherms and kinetics of the adsorption process. FTIR analysis was initially used to determine the surface functionality of adsorbent materials. Later, a batch adsorption of common pharmaceutical, Carbamazepine (CBZ), was conducted with different pH values (ranging from 1 to 12) to determine the optimal pH range for the adsorption procedure. This experiment established the following effective pH range: the maximum adsorption capacity of mixture of activated carbon and geopolymer powder and additively manufactured activated carbon based geopolymer is at pH 9, while the mixture of hydrotalcite and geopolymer powder requires a pH of 1, and additively manufactured hydrotalcite based geopolymer adsorbent requires a pH of around 2.5, as the 3D printed structure was not stable at high acidic conditions. Additional research is necessary to develop a stable 3D printed geopolymer adsorbent.

Kinetic analysis revealed that adsorption of CBZ by all the studied materials in this work followed the intraparticles diffusion model of adsorption. The adsorption isotherm analysis indicated the following maximum adsorption capacity: milled composite of AC and geopolymer 32.16 mg/g, AC-fabricated 3D printed geopolymer 100.198 mg/g, milled composite of hydrotalcite and geopolymer 10.97 mg/g, and hydrotalcite-fabricated 3D printed geopolymer 3.30 mg/g. The explanation for the decreased adsorption capacity of hydrotalcite fabricated 3D geopolymer was the pH range, since geopolymers perform optimally at pH 1. For powder geopolymer, the highest adsorption capacity was determined to be 0.075 mg/g at pH 2.

Generally, it can be concluded that additively manufactured AC geopolymer has a very good potential in the removal of pharmaceuticals from the wastewater and further studies with other kind of pollutants should be conducted. In addition, it would be highly important to optimize the 3D-printed structures and compositions to increase their stability and efficiency further. In order to make pilot scale studies scaling of the printing technology is required. 3D-priting is becoming more and more popular in separation and purification technology and therefore, the presented research can be used as a steppingstone for the related innovations in the future.

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