An-Najah National University
Faculty of Graduate Studies

THERMALLY STABLE MONTMORILLONITE/ SAND COMPOSITE FOR THE REMOVAL OF PHENAZOPYRIDINE FROM WATER BY ADSORPTION, FOLLOWED BY THERMAL REGENERATION: REUSABILITY IN BATCH AND CONTINUOUS FLOW SYSTEMS

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Dedication

To my beloved mother and father

Your endless love, prayers, sacrifices, and efforts make everything I have achieved possible…

To my dearest brothers who supported me…

To all my teachers who taught me…

to my future family…

I dedicate this work.

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Thank God, first and last, who granted me strength, guidance, and success to complete this work.

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I would also like to extend my heartfelt thanks to my family for their support, who encouraged me and shared the challenges of this journey with me.

And to every individual and institution that contributed in any way to the success of this work.

Declaration

I, the undersigned, declare that I submitted the thesis entitled:

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I declare that the work provided in this thesis, unless otherwise referenced, is the researcher’s own work, and has not been submitted elsewhere for any other degree or qualification.

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Signature:

Date: **23/06/2025**

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Abstract

Water pollution caused by pharmaceutical contaminants has become a serious global issue, mainly due to industrial growth and improper waste disposal. This study proposes an effective, eco-friendly, and low-cost method for water purification from phenazopyridine hydrochloride (PHY) using the prepared adsorbent montmorillonite/sand composite (Mnt/sand) combining adsorption with thermolysis technique for adsorbent regeneration.

The Mnt/sand composite was applied in both batch and column systems. In the batch system, several parameters were optimized. The adsorption performed best in acidic medium at pH 5, and was also relatively efficient at neutral pH. Adsorption efficiency decreased in highly basic conditions. Optimizing other parameters improved removal efficiency, with 0.5 g of adsorbent removing 96% of a 100 mL, 20 ppm PHY solution within 20 minutes at 25°C.

The Langmuir isotherm model ($R^2 = 0.99$) best fits the adsorption data, indicating monolayer adsorption on a homogeneous surface. Kinetic studies showed that the process followed a pseudo-second-order model, and the activation energy was calculated to be 30.4 kJ/mol. Thermodynamic analysis revealed that adsorption was spontaneous and endothermic, suggesting a strong interaction between PHY and Mnt/sand.

Column studies investigated factors like flow rate, concentration, temperature, and column height. Lower flow rates and concentrations improved performance, and taller columns enhanced efficiency. Optimal parameters were determined to be: 10 mL/min flow rate, 50 ppm concentration, 6 g adsorbent, 8 cm column height, pH 5, and 25°C achieving 97% removal efficiency.

Characterization techniques such as XRD, SEM, TGA, and FT-IR confirmed the structural integrity, porosity, and thermal stability of Mnt/sand. FT-IR confirmed PHY adsorption and successful removal after thermolysis. Thermal regeneration was achieved by heating the contaminated adsorbent to 650°C, decomposing PHY into CO_2, H_2O, and volatile gases without damaging the adsorbent, and maintain the adsorption efficiency for 6th cycles of reuse. Computational studies confirmed that reducing the thermolysis temperature to 550°C maintained performance, saving energy.

In conclusion, the adsorption-thermolysis method using Mnt/sand is a practical, efficient, and reusable approach for removing pharmaceutical pollutants from water in both batch and continuous systems.

Key words: Adsorption; Adsorbate; Adsorbent; Montmorillonite; Sand; Phenazopyridine hydrochloride; Column system; Batch system; Thermal decomposition.

Chapter One

Introduction

1.1 Overview

The health of every living creature on the planet depends on the purity of the water, therefore, the water sources are becoming more and more polluted due to the world's growing population, manufacturing, development, and chemically enhanced agricultural activities [1]. Water pollution is an international concern, caused by various contaminants that are released directly or indirectly into water sources such as rivers, lakes, seas, and other water bodies, negatively affecting the quality of water, consequently causing a serious threat to human health and the environment [2].

Water can be polluted by different types of pollutants, such as heavy metals, nutrients, and salts, which are classified as inorganic pollutants. In addition, pesticides, industrial dyes, pharmaceuticals, and personal care products, as organic pollutants, also include petroleum products such as oil, gasoline, and grease [3]. These varied types of water contaminants can be introduced into water sources mainly from industrial discharge, sewage, fertilizers, animal waste, disposal of unutilized medications, oil spills, and other sources [4]. The variety of poisonous pollutants and their multiple sources make this problem more severe and challenging.

Ecosystems and human health are the most harmfully affected by water pollution, having dire consequences for several areas. Human consumption of contaminated water can cause health problems such as cancer, growth issues, brain diseases, and other diseases, which can lead to death [5]. These pollutants also extend to agricultural infrastructure and marine life, which poses a danger to the lives of plants and organisms living in this environment, threatening biodiversity. In addition to affecting the food chain when these contaminations accumulate in organisms moving up to humans and predators who consume these animals [6]. Given its spread and danger, there is a justified need for efficient, practical, simple, eco-friendly technologies, using reusable and highly stable materials to deal with these pollutants, which is of great importance [5, 6].

1.2 Pharmaceutical Pollutants

Pharmaceutical pollutants have become a part of both the industrial revolution and medical advancement, and because of their own ability to affect human physiology at low dosages, they represent as a unique class of emerging environmental hazards when they are wrongly present in the environment [7]. Human elimination, pharmaceutical industry effluents, livestock and farming waste, incorrect disposal, and hospital effluent are examples of ways that these pollutants can be transported to the environment [8]. In the 1980s, the appearance of pharmaceuticals in the natural environment was first detected [6]. Recently, 44 of the most significant medications associated with the water cycle have been listed, based on their occurrence, toxicity, physicochemical characteristics, resistance to treatment, and persistence of consumption [9].

The environmental impact, genotoxicity, and serious toxicity of pharmaceuticals and their derivatives have attracted increasing attention from scientists. They can affect both aquatic and plant life by contaminating the water and soil [10, 11]. With their diffuseness and environmental hazards, a sustainable method for treatment has become essential, citing evidence from many associated studies that have indicated how resistant they are to traditional purification methods. That makes them one of the most significant environmental pollutants, posing a challenge to researchers[9].

Due to the common use and abundance of pharmaceuticals, which magnifies the potential environmental risks, a complete study is urgently required to provide a proficient, sustainable, workable, and cost-effective purification method for pharmaceutical-contaminated water [8].

1.2.1 Phenazopyridine

Phenazopyridine is a pharmaceutical contaminant that can be used as a model to address the environmental danger resulting from these pollutants. The presence of phenazopyridine in waterways emphasizes the challenges of managing antibiotic remains. It has a significant contribution to environmental pollution, as a result of unchangeable discarding through urine and feces, maintaining its structure consistent after performing its biological role within the body [12].

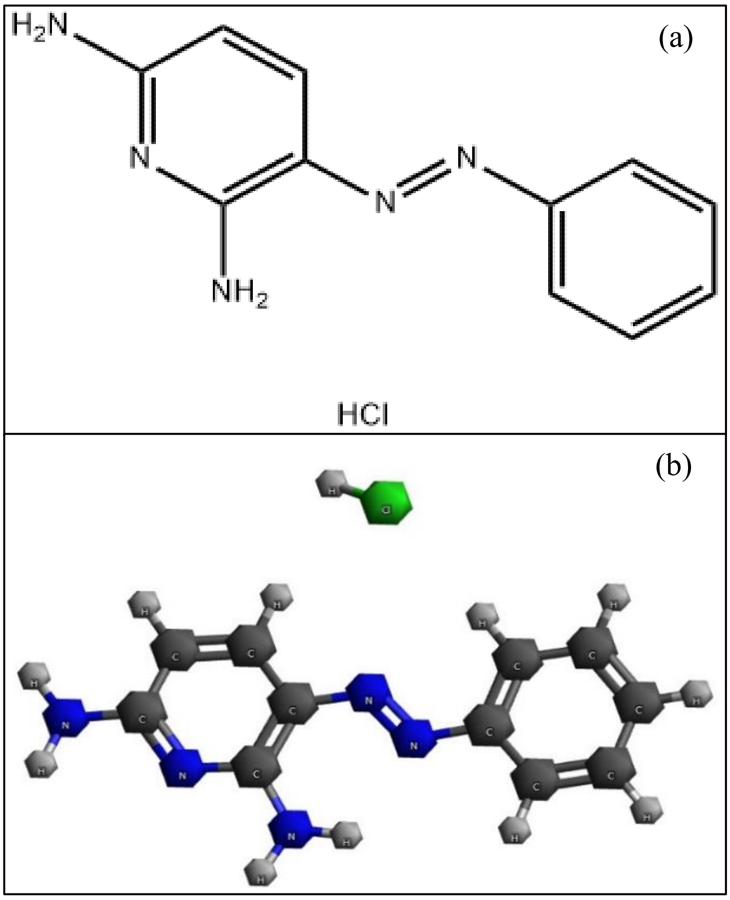
1.2.1.1 Phenazopyridine Chemistry and Uses

As a pharmaceutical, phenazopyridine, IUPAC-named 3-phenyldiazenylpyridine-2,6-diamine hydrochloride, is a heterocyclic aromatic azo-derivative dye. Phenazopyridine, a reddish brick microcrystal with a lightly violet shine at room temperature. Because of its bright red color, it can additionally be utilized as an indicator of pH in analytical chemistry [13].

Phenazopyridine Fig.1.1 is an organic compound with a molecular formula of $C_{11}H_{11}N_5$, with a molecular weight of 183.22 g/mol, has a pKa value equal to 5.2, which is considered a weak base, therefore its protonated with H+ below pH 5.2 and shows high solubility in water, and mostly neutral above this point, that affect its interaction with other material.

Figure 1.1

Phenazopyridine structure



Note: (a) structural formula of phenazopyridine hydrochloride, (b) skeletal formula of phenazopyridine hydrochloride.

Phenazopyridine has been used widely in medicine as an analgesic drug to relieve pain, discomfort, and the feeling that one must urinate regularly or urgently related to urethritis, cystitis, and urinary tract infections. As a dye, it calms the urinary tract coating by acting as a pain soother [14]. The pharmacokinetic properties are poorly recognized. However, N-acetyl-P-aminophenol (acetaminophen), P-aminophenol, and alanine have been found in the urine as Phenazopyridine metabolites [15].

Phenazopyridine is primarily excreted through urine, making it a common contaminant in wastewater treatment plants. It is also found in surface water bodies due to improper disposal of pharmaceuticals and industrial effluents [16].

1.2.1.2 Phenazopyridine Environmental and Health Concerns and Regulations for Drinking Water

Phenazopyridine leakage into wastewater treatment plants stems from multiple primary sources. They mainly come from urine, which contains phenazopyridine and its metabolites, in addition to improper disposal procedures of Phenazopyridine drugs and their industrial residues, making them spread in water bodies. As a result, the watery environment suffers numerous impacts and poses a danger to aquatic life, regarding the direct harm to the liver and other organs caused by phenazopyridine compounds. This was supported by earlier research on rats and mice that had continuous consumption of phenazopyridine, results showed the presence of large-intestine cancers [17].

On the other hand, accidental consumption of phenazopyridine by humans through contaminated water sources could end up with negative health symptoms such as headaches and stomach disorders. A significant yellow coloring may appear on the skin and eyes. In addition, Hemolytic anemia and methemoglobinemia have been observed as a result of direct consumption through therapeutic and excessive doses. Pale skin, fever, weakness or confusion, swelling, weight gain, dyspnea, blue or purple skin, etc., are some of its major side effects [18]. Consequently, to prevent the health hazards mentioned, it is essential to remove any residues of phenazopyridine from water sources.

1.3 Treatment Methods

The increasing concerns about the spread of pharmaceutical chemicals in water sources are justified due to their widespread use in human activities and their incorrect disposal, which demands the provision of proper treatment methods. Since traditional methods for treating polluted water are primarily available, they face resistance from pharmaceutical chemicals. Therefore, there is an urgent need to provide environmentally friendly, economical, and highly effective long-term methods [19].

The purification techniques are divided into three primary classes: chemical (ozonation, Fenton oxidation, ionizing radiation), physical (activated carbon, graphene/graphene oxide, carbon nanotubes, membrane filtration, ultraviolet), and biological (activated sludge, algae-based technology, membrane bioreactor, and photo technology) [19].

Advanced oxidation processes (AOPs) have been used in pharmaceutical removal from water, they depend on generating highly reactive hydroxyl radicals so they can degrade the pharmaceutical molecules to less toxic substances, as Wols and others did with a list of selected pharmaceuticals using the degradation method by UV/H_2O_2 [20]. Also, a group of pharmaceuticals like the antineoplastic drug (CPD), trimethoprim (TMP), and antibiotics ciprofloxacin (CIP) have been treated from water through AOP technology $UV/H_2O_2/O_3$, and its assistant processes. AOPs are even effective for a wide range of pharmaceuticals, but they can be energy-intensive and need a pretreatment procedure [21].

Membrane filtration as a physical method, mainly relies on pore size membrane that can physically separate contaminants, but for pharmaceuticals removal, it's difficult to predict the efficiency due to its complex mechanism that depends on the physical and chemical properties of the contaminant, in addition to that for membrane, as molecular weight cut-off, zeta potential, influent matrix, and solute-membrane interactions. One of the membrane's limitations is that it is susceptible to damage, making it challenging for reusing applications [22]. Snyder et al. have applied several membrane types for removing pharmaceuticals from water (such as ibuprofen, iopromide, diclofenac, and others), including ultrafiltration, microfiltration, reverse osmosis, nanofiltration, membrane bioreactors, electrodialysis reversal, and combinations of membranes in series [23].

Biological methods have also been used, like activated sludge [24], and membrane bioreactors [25], which degrades pharmaceuticals utilizing microorganisms, which makes it eco-friendly and cost-effective; however, it consumes a long time, also it's limited to a few ranges of pharmaceuticals [26].

Adsorption is a common and effective method that relies on large surface area materials that can adsorb the pharmaceutical pollutants on their surface, directly removing them from water. A widespread adsorbent like activated carbon, carbon nanotubes (CNTs), biochar, metal-organic frameworks (MOFs), and zeolites have been used for pharmaceuticals elimination from water [27]. Adsorption simplicity, cost-effective, and high efficiency present it as a promising solution for water purification from pharmaceuticals pollutants, however, the disposal of the adsorbed contaminants may be ineffective for some pharmaceuticals, observing a stiffness in the ability to reuse adsorbent material, such as CNTs that was used for tetracycline, amoxicillin, penicillin G, and cephalexin elimination from aqueous solution [28].

1.4 Adsorption

Adsorption is a phenomenon described as a surface process due to the superficial contact between either a solid, liquid, or gaseous substance, called the adsorbate, and the surface of an adsorbent, driven by forces arising between the adsorbate and adsorbent surface [29]. Multiple systems of adsorption exist based on the type of phases that are in contact, including liquid-liquid or liquid-gas, which indicate the presence of a liquid material as an adsorbent. On the other hand, when the adsorbent is solid, the system is considered a solid-liquid or solid-gas system. On a large industrial scale, the development of adsorption processes mainly focuses on solid-liquid and solid-gas interfaces. The phrase "fluid" is often used to describe a gas or liquid that comes into contact with a solid boundary surface [29].

The mechanism of adsorption, which can be a physical or chemical process, takes place when the adsorbate adheres to the adsorbent surface, causing a concentration change of the adsorbate at the interface compared with the surrounding phases. More specifically, the equilibrium among the adsorbent bores and bulk molecules is described as the interfacial layer, this layer is composed of two zones (in terms of solid-gas interface): the surface of the solid layer and that part of the gas that is contained within the solid's force field.

There are two principles provided as explanations for this mechanism, both mechanisms can take place simultaneously or independently under favorable conditions.

- Physical adsorption: Vanderwall's forces are mainly responsible for the weak interaction between the adsorbate and adsorbent in physisorption. It is a reversible process, with the ability to have multilayer adsorption.
- Chemical adsorption: A strong attraction between the adsorbent's surface and the adsorbate is represented by an electronic bond (covalent or ionic bond). It often has an irreversible mechanism. Contrary to physisorption, chemisorption only takes place as a monolayer [30].

1.4.1 Adsorption Features

There is no doubt about the significance of adsorption with regard to technology, the environment, and biology. Furthermore, this also involves its importance in treating and purifying water, soil, sewage, and air. In addition, a lot of catalytic processes begin with the adsorption of substrates [31].

The adsorption method is recognized to be appropriate for wastewater treatment, whether it works on organic, or inorganic pollutant, the credit for that goes to the characteristics it possesses, including simplicity of operation offering a practical option for either large-scale or small-scale water purification application, high efficiency of removal (most common are activated carbon, nanomaterials, biochar, clay) [32]. Selectivity of removal, which can be improved by different modifications, enhancing their efficiency for capturing targeted pollutants, such as polymeric adsorbents [33], and the ability of regeneration for many adsorbents by different methods involves thermal regeneration [34], chemical washing, electrochemical regeneration, biological degradation, and other methods, making it a sustainable and reusable technique [35].

1.4.2 Parameters Affecting Adsorption

The adsorption process is controlled by many chemical and physical factors, such as:

1. The surface area of the adsorbent.
2. Adsorbent amount used for adsorption.
3. The surface chemistry and functional groups of the adsorbent.

4. Adsorbent particle size: A smaller particle size is needed to reduce adsorbate mass transfer in the adsorbent, which achieves easier equilibrium and provides more attainable adsorption.
5. Initial concentration of adsorbate solution.
6. pH of solution: Adsorbate affinity to adsorbent is affected by the nature of the adsorbate (charge, ionization, solubility) and the surface chemistry of the adsorbent
7. Contact time: When adsorbent and adsorbate are in contact for longer time, more completeness is achieved for adsorption.
8. Temperature [6, 36, 37].

1.4.3 General Adsorbent Needs

The selection of an adsorbent for polluted water treatment depends on multiple factors, the most significant of which is surface area, which must be large, providing abundant pores and sites to bind with adsorbate molecules, as well as surface chemistry of the adsorbent involving polarity, surface charge, and elemental composition. Other crucial features are thermal stability, corrosion resistance, and the ability to regenerate of adsorbent, making it sustainable and long-term usable. In addition, it should be cost-effective, easily available, and non-toxic. Also, considering the chemical and physical nature of the contaminant is critical, such as polarity, functional groups, charge, chemical reactivity, solubility, and others, in addition to its concentration (pollution level), presence in the aqueous solution [38].

1.4.4 Adsorbents Used to Remove Pharmaceutical Compounds from Wastewater

In water treatment, it has been proven that adsorption can be successfully used in removing organic compounds and heavy metals [39]. When it comes to pharmaceutical compounds, adsorption is among the record methods for eliminating them from wastewater. Moreover, many adsorbents have been developed and investigated to enhance the adsorption capacity of pharmaceutical compounds [40].

There is a large variation in the substances that can work as adsorbents to remove pharmaceutical compounds from wastewater, as Wei and Deng established the use of granular carbon nanotubes/ alumina hybrid adsorbents for diclofenac sodium (DS) and carbamazepine (CBZ) removing [39], activated carbon (including powder, granules, fabrics, and fibers) has also shown a role in pharmaceuticals treatment, which was performed in Lladó work including an equilibrium and kinetics investigation for atrazine and paracetamol adsorption on activated carbon [41], Graphene and graphene oxide [42] ion-exchange resins [43], biochar that is prepared by pyrolyzing biomass and then treated with acid to activate it [44], Agricultural waste [45] Synthetic adsorbents as modulated Polymeric materials [46] Magnetic adsorbents [47] clay and clay derivatives [48].

1.5 Clay

Clay is one of the natural materials composed mainly of fine-grained minerals, which are almost hydrous aluminum phyllosilicates and various quantities of other ions, depending on the type of clay [49]. Clay has special features such as small particle size (less than 2 microns), and a unique crystal structure, in addition to its abundance, which provide it with crucial applications in different fields, including the use of clay as an adsorbent for water purification [50]. Clay or hydrated alumina silicate, as it is named, also has high mechanical and thermal stability, Low permeability, high sorption capacity, and a large surface area [51].

The involvement of metallic or nonmetallic elements and variation of porous structure and sizes results in multiple types of clay, which possess different probabilities [52]. Also, the mechanism applied in removing emerging contaminants obviously affects the adsorption capacity [48, 53].

The individual Layers involved in clay minerals consist of tetrahedral (T_h) and octahedral (O_h) sheets in a 1:1 or 2:1 ratio. The layers of many tetrahedral form clay minerals (such as the smectite group and Vermiculite group) hold an invariant negative charge due to isomorphism phenomena in the tetrahedral sheet, in particular Si^{4+} substitution by Al^{3+}. This deficiency in positive charge generates a negative charge, which is counterbalanced by cations occupying the interlayer space. That asserts the effectiveness of clay minerals for cationic contaminants adsorption [54, 55].

In contrast, modified clay can be worked as an adsorbent for a wide variety of contaminants. Modifications such as thermal treatment and acid washing can enhance the capacity of broad contaminants [56-58].

1.5.1 Clay and Pharmaceutical Adsorption

For aqueous dissolved organic contaminations, a current water treatment method, such as adsorption on natural clay is regarded as one of the most efficient and reliable methods [5, 59], which has been used in dye removal from aqueous solution, with regards to the strong affinity of clay minerals for heteroaromatic cationic dyes, such as smectites and zeolites that were used for methylene blue removal [60]. In addition, it was applied to pesticide water treatment, as Pusino and others presented in their work using the Cu^{+2}, Fe^{+3}, and Al^{+3}-saturated montmorillonite for diclofop and diclofop-methyl adsorption [59].

Clay has been shown to play a significant role in successfully removing pharmaceutical compounds from aqueous solutions [5, 27]. Montmorillonite, kaolinite, and bentonite are the most common types of clays used in pharmaceutical adsorption from water. The last studies showed a high-efficiency performance of clay for various pharmaceutical pollutants such as ciprofloxacin hydrochloride, amoxicillin, ampicillin, enrofloxacin, paracetamol, levofloxacin, gemifloxacin, tetracycline, carbamazepine, and caffeine, with rate removal percent ranging from 42% to 99%, where the montmorillonite is ranked first, followed by kaolinite which sometimes above 95% percent of removal, and bentonite is coming third showing good adsorption capacity, especially with a surfactant modifications [27].

Moreover, clay has been investigated as a high thermal stable adsorbent, making it resistive to thermal regeneration methods such as thermolysis that was used in regenerating organic contaminated clay, maintaining its mass above 1000 ◦C [34]. Compared with other adsorbents like activated carbon, it start damaged and loss mass at temperature between (500-600◦C) [61]. These clays, either in their modified or natural form, have shown promise as reliable and effective adsorbents for pharmaceutical purification and eco-friendly uses, according to their physical and chemical properties [5].

An innovative method was developed by Zyoud et al. for the purification of water contaminated with tetracycline, a pharmaceutical pollutant, using montmorillonite clay as an adsorbent. This method leverages the high thermal stability of montmorillonite, as confirmed by thermogravimetric analysis (TGA), which showed a constant mass up to

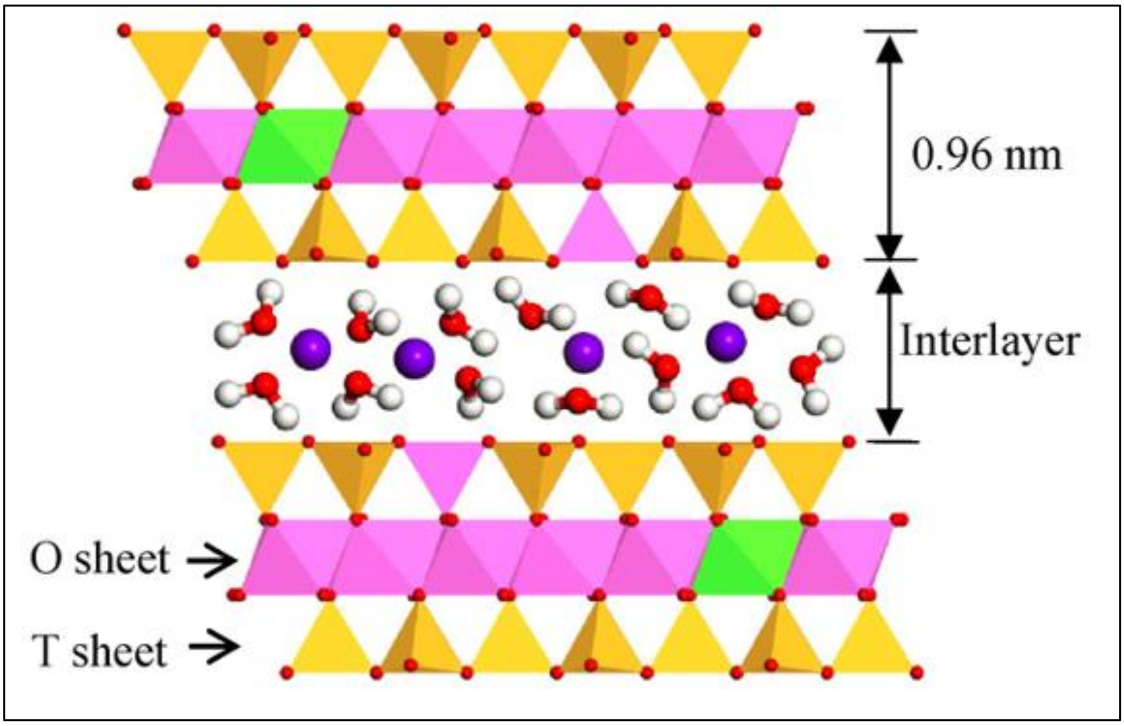
1000 °C. A novel thermolysis technique was introduced for regenerating the used adsorbent, representing a new water purification technology unique to Zyoud [34]**.** This technique was applied in a batch system, which requires further investigation for practical, continuous-flow, and large-scale applications—an objective addressed in the present work.

1.5.1.1 Montmorillonite

Montmorillonite is an aluminosilicate layered clay mineral with a molecular formula $Al_2O_3.4(SiO_2).H_2O$ [62], Montmorillonite clay is a part of the smectite group [63]. It is a typical clay mineral of the 2:1 type, with each octahedral sheet lined between two tetrahedral sheets. The isomorphous exchange by Mg^{2+} for Al^{3+}, and by Al^{3+} for Si^{4+} Mainly raises the negative charge in the octahedral sheet, which has 0.2-0.6 charge density per half-unit cell. This negative charge appearing from isomorphic substitution gives montmorillonite a fundamental property controlling its adsorption mechanism, such that it attracts the positive species charged through electrostatic forces (hydrogen bonding, dipole-dipole interactions) or even ion exchange, making it suitable as an adsorbent material for cationic contaminants and pharmaceuticals [64].

Figure 1.2

Montmorillonite structure



The following are Montmorillonite's advantages as an adsorbent:

1. Montmorillonite can be used as a highly effective adsorbent for many types of cationic contaminants according to its layered structure.
2. Montmorillonite is a high thermal stability, low price, eco-friendly, widely distributed, and abundant material.
3. Montmorillonite-based adsorbents generally have a larger adsorption capacity compared to their analogs, due to their high surface area.
4. Associated adsorption mechanism of montmorillonite-based adsorbent, generally applicable to their counterparts [55].

However, due to the hydrophilicity of montmorillonite, it has a weak adsorption effect with hydrophobic organic compounds [65]. Because of this, the following modification has been improved. Presently, ammonium cationic surfactants are commonly employed as modifiers, achieving quick adsorption and high capacity for Ibuprofen adsorption. Another modification for silica nanosheets including montmorillonite, Zeng et. al. combined montmorillonite with varying alkyl chain lengths of gemini surfactant, resulting in high adsorption capacity and instant adsorption property for a low concentration addition of surfactant; however, longer alkyl chains present a lower adsorption capacity with more adsorbate removed [66]. The experimental results of Adosantos et. al.'s work show a significant adsorption capacity for P-nitrophenol when applied a modification on montmorillonite with acetyl trimethyl ammonium bromide (CTAB) [67]. Where Marina et al. used stearyl trimethyl ammonium as a modifying agent for montmorillonite and applied it to multiple pharmaceutical contaminants, such as carbamazepine, ibuprofen, and paracetamol, they obtained an adsorption capacity of 97%, 95%, and 67% with initial concentrations ranging from 10 to 50 mg/L [68]. Another method of activating the montmorillonite is acid activation, as it was applied for pyridine adsorption on acid-activated montmorillonite clay. In addition to organo-modifications and acid activation, metal oxide can also be used to improve the stability and selectivity of montmorillonite for specific applications [69]. Other studies authorized its use without any further treatment, as Wane et al. have reported the Enrofloxacin adsorption on pristine montmorillonite at concentrations ranging between 1.16-6.68 mmol/L with an adsorption capacity of 667mg/g [70], asserting its validation as an effective adsorbent.

According to the literature review, Montmorillonite is the most generally assessed clay mineral for the adsorptive removal of pharmaceutical Compounds. Referring to the studies that examine clay minerals as adsorbents for pharmaceuticals from aqueous solution [27]. Most of these previous studies depended on the batch system technique for the montmorillonite adsorption study. On the other hand, according to our knowledge, there is a gap between Montmorillonite and large-scale water purification applications, such as the column system technique, as these studies are very limited [71]. That is due to its particle size (fine powder material) and morphology makes it resistant to the smooth flow of the aqueous solution through its pores, therefore, the montmorillonite particles in the fine powder form cause a pressure drop in the column, preventing the solution from passing out of it. Nevertheless, pelletization or granulation can be applied to optimize the column performance of the montmorillonite using a suitable supported material (such as silica sand), which is considered in this work.

1.6 Sand

Sand is a type of soil particle with a granular shape and a diameter ranging between 0.05 and 2.0 mm. It can be found in nature as very fine sand, fine sand, very coarse sand, coarse sand, medium sand, coarse sand, and very coarse sand [72]. However, sand can be composed of finely separated mineral particles; the most found mineral in sand is quartz (SiO2). According to the geological source and environment of the sand, other minerals, such as mica, feldspar, and calcite, could also be present [73].

Sand grains form when stones erode and weather over thousands and even millions of years, due to factors like wind, water, and ice [74]. Most sand beaches tend to have a tan color due to iron oxide, which gives quartz a light brown tint, in addition to feldspar, which is actually brown to tan [75]. Various types of sand, such as sea beach sand, which is usually made up of quartz grains, are often combined with broken shells and other trash. Quartz grains compose the majority of desert sand, but feldspar and other minerals may also be present. A combination of different minerals, such as mica, feldspar, and quartz, generates river sand [76].

Due to its sub-round to the round shape, silica sand (silica in the form of quartz grains makes up the majority of its composition) is a perfect filtration medium for removing suspended solids from water [77]. The sand's high silica content makes it extremely hard and sustainable. In addition, its abundance, affordability, and accessibility in nature make it a good choice for filtration purposes, as it was used in the past, but its efficiency was quite low [78]. However, using it as a supported material for another adsorbent material is most widely applied in the present studies, especially for nano-adsorbent materials [79, 80].

1.7 Clay Composites

1.7.1 Nanocomposite

Nanoparticles have a set of unique chemical and physical properties. Compared to macroscopic particles, nanoscale materials such as clay, zeolites, ceramics, polymers, and carbon derivatives (carbon nanotubes) at the nanoscale have a larger ratio of surface area to particle size and as well as different electrical, optical, and magnetic properties [81].

On the other hand, the stability decreases as the size is diminished from micrometers to nanometers due to the surface energy increasing. Consequently, it will often agglomerate as a result of some interactions, mainly Van der Waals forces, forming micrometer particles such as montmorillonite, zeolites, and other clays. To improve the usability of these materials in real wastewater treatment, they are combined with other matrices, mainly polymers, to obtain nanocomposite adsorbents such as polymer-clay nanocomposites [32].

Nanocomposites have applications in various sectors, including water purification. However, it causes a significant drop in mechanical strength and pressure, making nanoparticles ineffective in flowing systems such as column filters. So, to generate a usable application of nanoparticles, mainly clays, in real treatment wastewater, it should have a consolidation from other supported materials to provide integrity and permeability, which can be used in many applications, in particular, large-scale water purification purposes [32].

1.7.2 Sand-based Composite

Adsorption-filtration is among the most straightforward, effective, and economical methods for treating wastewater. However, it is critical to select the correct type of adsorbent/filler. Therefore, there is an essential need to develop an effective and economical technique to remove pharmaceuticals before they are introduced into water sources from wastewater flows.

Sand-based composites can be used in the adsorption filtration technique, where the sand is used as the supported material of this type of adsorbent due to its permeability, availability, cheapness, and abundance in the crust of the earth. Even though powdered materials based on sand itself have already been used for water purifying purposes, however, the efficiency of these materials was very low [77]. For instance, the efficiency of sand-based adsorbents has been enhanced by some researchers by inducing effective materials such as iron oxide, graphite oxide (for Pb) [79], manganese oxide (for Cr)[80], and ferrihydrite (for As)[82] as a capturing agent on the sand, which concentrated on inorganic elements.

The adsorption capacity of sand-based adsorbents for organic compounds was therefore considered to be improved by the addition of biochar, xanthan gums, guar gum, bentonite, and sodium alginate. Any of the mentioned binding agents could improve the sand-based adsorbents' surface and structural characteristics [83].

1.8 Fixed-bed Column

The formation of the fixed-bed column, as an adsorption technology, is the binding of an adsorbent material in a container to form an adsorption bed. The target contaminant molecules are adsorbed on the bed as the contaminated fluid flows directly through the column [84]. Batch systems in wastewater treatment often lack practical use due to insignificant contact times for equilibration [85]. Subsequently, fixed-bed adsorption offers economic advantages by assuring interaction between the contaminant and the adsorbent, leading to effective performance. For the adsorption application of various pollutants, this technology shows high adsorption efficiency, adsorbent usage, and controlled processes. Many Factors affect the efficiency of the column adsorption system, including flow rate, column height, adsorbent particle size, and others, which must be optimized to get high adsorption efficiency. Whereas the ability of regeneration and reuse is most important in this technique [65].

Fortunately, the nanomaterial can be rinsed away and is challenging to separate for reuse and recycling, making it hard to pack in a column. Consequently, support material is necessary to place nanoparticles in a fixed-bed column. As mentioned previously, sand-based adsorbent is highly recommended in the adsorption filtration column technique due to its porosity, chemical and thermal stability, and cost-efficiency. Additionally, it plays a role in enhancing the surface area of the supported adsorbent material for increased adsorption capacity [86].

In addition, traditional adsorbents like NPs, ACs, and ZVIs cannot be used commercially on a large scale because of their high cost and complicated synthesis process [87]. The spotlight has recently been put on advancing natural adsorbents with a high capacity for removal, non-toxic nature, thermal stability, and sustainable properties (such as montmorillonite clay) to enhance the removal performance of large organic compounds (such as pharmaceuticals) from water resources. Therefore, using the sand-based adsorbents in a fixed column has the potential to be suitable and effective for organic compounds and pharmaceuticals elimination.

1.8.1 Experimental Parameters of Column Adsorption

1. The initial concentration of contaminants.
2. Flow rate of solution through the column.
3. Temperature of solution.
4. Height of column.
5. Thermolysis temperature for columns.
6. Initial pH of solution [79].

1.9 Novelty of this Work?

Surface water contamination by pharmaceuticals has grown to be a major worldwide concern. While most repeated studies assert that montmorillonite is the most effective and suitable for pharmaceutical adsorption, it goes without practical application, while sand, which shows negligible adsorption performance, has high applicability. Therefore, the combination of the high efficiency of the montmorillonite and the practicality of the sand-supported adsorbent will provide a promising purification method.

This work has the novelty of using a montmorillonite sand-based composite (Mnt/sand) as an adsorbent for the pharmaceutical contaminant phenazopyridine. The suggested adsorbent particles of (Mnt/sand) are predicted to fit a fixed column system, which is a practical, simple, cost-effective method, in addition to a batch system that will be studied.

The thermolysis decomposition process will be used to regenerate the used adsorbent, as a new technique for organic contaminated adsorbent regeneration, taking advantage of the organic nature of phenazopyridine, which breaks down into CO_2, H_2O, N_2, and other gases under thermal decomposition, leaving behind a clean adsorbent can be used multiple times for adsorption experiments. This will maintain the efficiency of the montmorillonite regarding its thermal stability as clay. Adsorption-thermolysis cycles using the (Mnt/sand) column will be used for the first time, looking forward to a sustainable, efficient, reusable, economical, and practical method for water purification from pharmaceutical pollutants.

1.10 Objectives of this Work

1.10.1 Strategic Objective

The overall objective of this work is to provide a sustainable and practical adsorption method for treating wastewater containing pharmaceutical pollutants (phenazopyridine as a model), using an efficient and low-cost adsorbent (Mnt/sand), which will be regenerated by thermolysis process to reuse it frequently, maintaining the efficiency of the adsorbent material.

1.10.2 Technical Objectives

This project studies two systems with specific objectives in mind.

Batch system

1. Treating and cleaning beach sand to increase its silica content.
2. Preparing the montmorillonite: sand-based composite (Mnt/sand) with a mass ratio of 2:8, respectively.
3. Characterization of montmorillonite, sand, and Mnt/sand using IR, XRD, TGA, SEM, and others before and after adsorption .
4. Studying the efficiency of prepared composite in the batch system for phenazopyridine (PHY) adsorption.

5. Study the effect of the parameters on the adsorption process, including Adsorbent amount, initial concentration of PHY solution, pH of the solution, Temperature of the solution, and adsorbent amount.

Column system

1. Sized the silica sand particles into specific ranges by sieving mesh in order to obtain the appropriate size range for Mnt/sand preparation.
2. Preparation of Mnt/sand.
3. Characterization of Mnt/sand by XRD, SEM, TEM, TGA, FT-IR.
4. Preparing column setup, using designed glass column, pump device, Mnt/sand, and solutions of contamination.
5. Parameters effect on continuous adsorption process study, such as flow rate, initial concentration, temperature of solution, Height of the column, and thermolysis temperature.
6. Regeneration and reusing columns.
7. Adsorption mechanism study for phenazopyridine on montmorillonite surface: a computational study.

Chapter Two

Materials and Methods

2.1 Chemicals and Reagents

The majority of the chemicals used in this research were purchased from Sigma Aldrich Chemical Company, which includes phenazopyridine hydrochloride (PHY) [136-40-3], montmorillonite (Mnt) [1318-93-0], and potassium chloride [7447-40-7]. Sodium hydroxide [1310-73-2], hydrochloric acid [1310-73-2], sulfuric acid [7664-93-9], and nitric acid [7697-37-2], were supplied +++by CS Chemical Company. Distilled water was used as a solvent for (PHY), which is the adsorbate model in this work, and the montmorillonite/sand composite (Mnt/sand) as the novel prepared adsorbent. The sand used in this work as a supporting material of Mnt was obtained from the Ashdod shore, Palestine.

2.2 Instrumentation

UV-Spectrophotometry (UV–Vis SHIMADZU UV-1800) was used for all spectral measurements. The pH was measured using a typical Jenway model: 35 pH meter. The samples were mixed and thermostatted by the Lab Tech water bath and shaker LSB-0. The separating process of adsorbent from the solution after adsorption reached equilibrium was done by centrifuging the LAB TRON LLS-A12 centrifuge in all batch experiments. In recovery experiments, contaminated Mnt/sand was thermally decomposed through the MRC Bench Top Muffle Furnace.

Characterization of solid material involving adsorbent and its components (Mnt, silica sand, and Mnt/sand), and adsorbate (PHY) was done by PANalytical X'Pert PRO X-ray diffractometer (XRD) equipped with CuKα (1= 1.5418 Å) and Jeol-EO Scanning Electron Microscopy (SEM) in AUE. Moreover, a critical characterization analysis of these samples (Mnt, silica sand, Mnt/sand, and PHY) was done using FT-IR (Thermo Scientific Nicolet iS5 FT-IR) at An-Najah National University in Palestine. For determining the decomposition temperature of adsorbate material (PHY), in addition to testing the thermal stability of adsorbent material (Mnt/sant), the thermogravimetric analysis (TGA) was applied by SANAF TGA.

2.3 Preparation of Standard Stock Solutions

A precisely weighed 1.0 g of PHY (M.Wt. = 249.70 g/mol) was dissolved in a 1000 ml volumetric flask and then filled with distilled water until adjusting the full volume, then with a digital ultrasonic bath, the solution in the closed 1000 mL volumetric flask was sonicated in order to prepare a clear and homogenous stock solution with concentration of 1000 ppm . PHY has a solubility (1.0 g/L at 20 ◦C) that is freely soluble at room temperature [88]. To prevent light exposure, aluminum foil was used to preserve the stock solution, which was then stored at room temperature until it was needed.

The working solution was prepared by pipetting 10 mL of the stock solution into a 100 mL volumetric flask. Following the addition of distilled water until the volume desired was reached, the flask was capped and gently shaken until the solution was homogenous, having a 100 ppm working solution of PHY (or adjusted to the required concentration).

2.4 Preparation of the Calibration Curve

A calibration curve describes the correlation between the absorbance of standard solutions at a particular wavelength, typically the maximum absorbance wavelength (λ max), and their concentration. In this investigation, standard solutions with concentrations ranging from 5 to 20 ppm were used to prepare a calibration curve, taking into account the deviation of Beer's law that tends to occur at high concentrations, low concentrations were picked in this experiment to get reliable and accurate results.

Aliquots of 5, 10, 15, and 20 ml of PHY working solution were taken by a pipette and transferred into four 100 ml volumetric flasks to create varied PHY solutions with concentrations of 5, 10, 15, and 20 ppm. Distilled water was then added to equalize the volumes to the fitting mark. Each solution's absorbance was measured by UV-Spectrophotometer at the maximum wavelength (λ_{max} = 425 nm) of PHY versus a blank of distilled water. The absorbance versus drug concentration was then plotted to generate the calibration graph. The linear formula of the calibration graph was used to calculate the unknown concentration of PHY solutions. The calibration graph's correlation coefficient (R^2) shows how strongly the variables are linear.

2.5 Preparation of Mnt/sand

2.5.1 Preparation of Mnt/sand used for Column System

A sample of beach sand was collected from the Ashdod shore in Palestine, and it was treated for use in the column experiments as a supported material of Mnt. Firstly, the sieving step was applied using the U.S. Alternative meshes to sort the sand by its grain size. Starting with a larger pore size mesh no.16 (>2.36 mm) to get rid of large stones and other trash, then with finer meshes no.30, giving a sand sample with particle sizes ranging between 600-1180 µm, which was used in this work. Secondly, the sand was washed with water to remove as many impurities as possible, and in a 1 L beaker, around 300 g of sieved sand (600-1180 µm) was added. Thirdly, the sand was reacted with concentrated nitric acid (1:2), added slowly to the sand, and an equivalent amount of concentrated hydrochloric acid was added, to remove any impurities such as carbonates, metals oxides or organic materials, leads to high silica sand form. The mixture was heated with stirring for 2 h and then kept overnight at room temperature. After being thoroughly cleaned with water to neutralize the contents, the high silica sand produced was dried for 2 h at 100 °C.

The adsorbent composite consists of two components, Mnt as effective adsorbent and silica sand as supported material, with a mass ratio of 1:4, respectively, where the amount of Mnt was sufficient to coat the sand grains and give a permeable composite to the liquid solution passing through it, which maintains a high water capacity on the one hand and absorption efficiency on the other[89-91]. In a 250 ml beaker, 20 g of Mnt with 80 g of prepared silica sand was mixed, followed by adding distilled water dropwise until a pasty granular texture was formed. Calcination of the Montmorillonite/sand composite (Mnt/sand) is applied at 550 ◦C for 2h, then it's cooled to be ready for utilization.

2.5.2 Preparation of Mnt/sand Used for the Batch System

The same procedure was applied to prepare the batch system adsorbent, except for the sieving step, which was overpassed, since there is no need to specify the size of the adsorbent particles in the batch system, on the other hand, the column system requires designing granules of a size that allows the flowing liquid to pass through, as very small granule sizes may prevent the liquid from passing and almost completely block the pores.

2.6 Mnt/sand Point of Zero Charge pHpzc

To prepare a potassium chloride (KCl) solution with a concentration of 0.1 M, 3.72 g of KCl was weighed accurately and dissolved in a 500 mL volumetric flask with distilled water. To have a homogeneous solution, the flask was capped with a stopper and shaken strongly, which assured complete dissolution of KCl.

Using the 0.1M KCl solution, seven samples were prepared in glass bottles with different values of pH. In each glass bottle, 50 mL of the KCl solution was transferred by a graduated cylinder. To adjust the initial pH of each sample, diluted solutions of HCl and NaOH were used, ending with a pH range of solutions that had the values: 2, 3, 4, 6, 8, 10, and 12.

Separately, 0.1 g of Mnt/sand was added to each bottle and locked tightly to be ready for the shaking step, which was applied in the shaker at 200 rpm at 25 ◦C for 24 h, allowing the solutions to reach the equilibrium point of pH. The last step includes measuring the final pH of each solution, monitoring the change in pH values required in the Mnt/sand point of zero charge calculation [92].

2.7 Adsorption Experiments

2.7.1 Batch System Adsorption Experiments

Batch experiments were used to investigate the adsorption of PHY onto Mnt/sand surfaces. A series of 100 mL capped urine cups was used for the experiments. The volume of PHY solution used in all experiments settled at 100ml, the effect of some parameters was studied in a batch system with diverse concentrations ranging between (10-50 ppm), initial pH (3.5-10), Temperature of solution (10-50 ◦C), amount of adsorbent (0.2-1.0 g). Every piece of used equipment was carefully cleaned beforehand using distilled water. The water bath and shaker was used to shake the experiment cups at 200 rpm after adding Mnt/sand to the PHY solution. The flasks were shaken continuously at a constant speed for one hour, and every 10 minutes, an aliquot was taken. The impure Mnt/sand was separated after adsorption reached equilibrium by centrifuging in all batch experiments. The amount adsorbed, the percentage removal, and the amount left can all be calculated from the initial concentration and the concentration at equilibrium, after centrifuging and measuring the absorbance of the supernatant by UV-Vis spectrophotometer. A certain amount of contaminated Mnt/sand was collected to reuse the adsorbent later. As previously mentioned, the mixture is centrifuged to collect the Mnt/sand once adsorption is complete. To complete thermal decomposition, a sample of tainted Mnt/sand was gathered in a crucible and placed in a furnace set at 550 ºC for two hours.

2.7.1.1 Effect of Initial Concentration

The aim of this study is to determine the rate of adsorption, the impact of contact time on adsorption, and the change in the concentration of adsorbate in the solution over time. In order to run the experiments, 0.5 g of Mnt/sand as a constant amount of adsorbent was added to 100 ml of a standard PHY solution with a constant initial concentration. The mixture was then capped in the cup and shaken contentiously at 200 rpm and 25 ◦C. Various aliquots of the mixture were taken every 10 min while shaking until equilibrium was reached (1h contact time), then centrifuged and analyzed using a spectrophotometer. The experiment worked on different PHY concentrations: 10, 20, 30, 40, and 50 ppm.

2.7.1.2 Adsorption Thermodynamics

In this section of work, it was investigated how temperature affected the adsorption process. Furthermore thermodynamic study was done to obtain thermodynamic parameters and their indication. PHY solutions were adsorbed by 0.5 g of adsorbent samples at pH 5. The mixtures were conducted at different temperatures: 10, 20, 30, 40, and 50 °C, shaken at 200 rpm for 1 h.

2.7.1.3 Effect of pH

The impact of the initial pH of the adsorbate solution on adsorption has been investigated in the pH range of 3.5 to 10. Adjusting the pH was performed by adding solutions of sodium hydroxide and hydrochloric acid to change the pH as needed. 0.5 g of Mnt/sand sample was added to each different pH solution of PHY in the urine cup (100 mL, 20 ppm). At 25°C, the mixtures were then shaken at 200 rpm for 1 h. The PHY maximum absorbance was measured in relation to λ_{max} at each pH.

2.7.1.4 Effect of Amount of Adsorbent

The adsorption study experiments were repeated after the equilibrium time was reached, but with different amounts of adsorbate. Moreover, the initial PHY concentration, pH, temperature, and speed of shaking were maintained at constant qualified values. The amount of PHY that adsorbs on different amounts of the adsorbent can be determined by adding: 0.2, 0.4, 0.6, 0.8, and 1.0 g of Mnt/sand to PHY solutions (100 ml, 20 ppm), shaking at 200 rpm until equilibrium was reached at 25 ◦C. The supernatant fluid concentration of remaining PHY was measured by the UV-Vis Spectrophotometer, and the percentage of removal can then be calculated.

2.7.1.5 Reusing of Adsorbent

In this work, the regeneration of contaminated adsorbent material has been implemented by the thermal decomposition process, which depends on the type of organic adsorbate that is adsorbed on the adsorbent surface. To determine the temperature of complete decomposition for PHY, thermogravimetric analysis (TGA) was applied on a sample of PHY, showing a loss of mass percent of the sample versus temperature. In addition, the TGA experiment of the Mnt/sand has been applied to ensure thermal stability under high temperatures reaching 800 ◦C.

For the reusing experiments, an amount of adsorbent was saturated with the adsorbate to reuse it later. As discussed previously, when adsorption is completed the Mnt/sand is collected after centrifuging the mixture. A sample of contaminated Mnt/sand was collected in a crucible and positioned into the furnace at 550 ◦C for 2h to finish off thermal decomposition. Regenerated Mnt/sand was cooled at room temperature, then first reused in a treatment run with a solution of PHY (100 ml, 20 ppm) by weighing 0.5 g of regenerated Mnt/sand and uploading it to the shaker at 200 rpm at 25◦C for 1h, after mixing in a urine cup. The previous step was repeated another three times to indicate the reusing efficiency of Mnt/sand as an adsorbent in the batch system experiments.

2.7.2 Column System Adsorption Experiments

In this study, a continuous adsorption system was performed with a fixed-bed column made of glass featuring an outer diameter of 12 mm, an inner diameter of 10 mm, and a length measuring 10 cm. The column is backed with Mnt/sand, which was prepared and designed to be convenient for column application. Glass wool was put in as support at the bottom and top of the column to prevent the falling or rinsing away of the backed Mnt/sand during transformation and regeneration processes. Four parameters were studied in the column system including initial concentration (20, 30, 40, and 50 ppm), flow rate (2, 4, 6, 8, and 10 mL/min), height of bed (4, 8 cm), and temperature of working solution (10, 20, 30, 40, and 50 ◦C). Moreover, thermal decomposition at different temperatures was investigated, which was supported by a computational study.

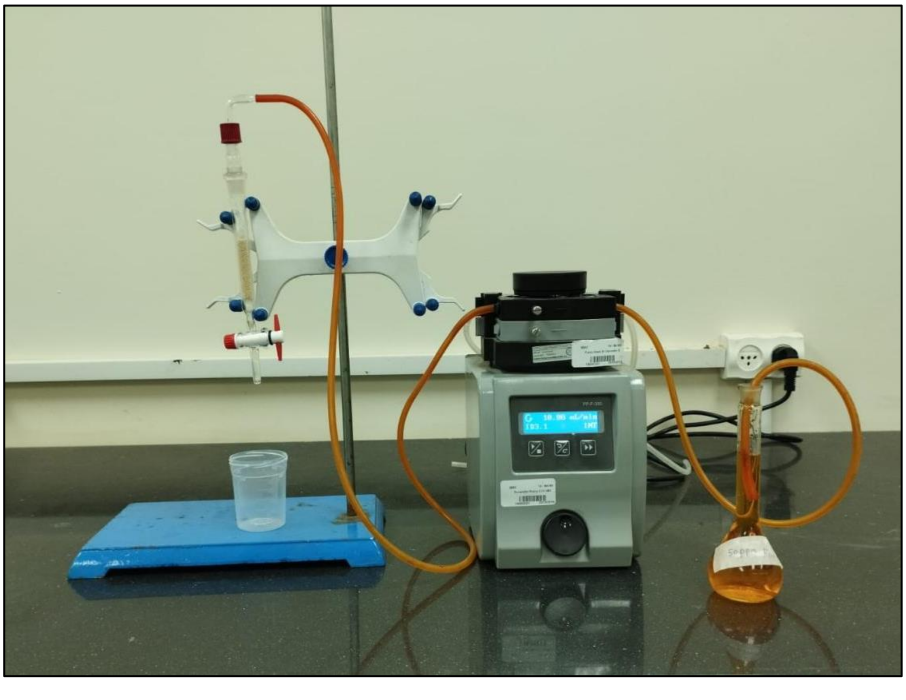
2.7.2.1 Preparing Column Experiments Setup

Continuous adsorption experiments were conducted in the Mnt/sand filtration column, which coupled with a peristaltic pump (LONGER), secures a precise flow rate for the influent solution. Working solutions (influent) were introduced into the column from the top by the pump tube, and the exiting solution (effluent) samples were collected from the bottom and were directly analyzed by the UV-vis spectrometer when the working solution was pumped out of the used column, it would be ready for recovery by the thermal decomposition process**,** allows multiple reuses of the same column for extended adsorption-regeneration cycles.

The setup of the column system needs some additional tools, such as the volumetric flask containing the PHY working solution, the tubing connected with the peristaltic pump, the metallic stand with burette clamp where the column was fixed on, the glass column backed with Mnt/sand granules, graduated cylinder where the effluent was collected at the bottom of the column.

Figure 2.1

The column system (continuous adsorption system) setup



2.7.2.2 Effect of Initial Concentration

The effect of the initial concentration of the influent solution was done by preparing four different concentrations of PHY solution 20, 30, 40, and 50 ppm in a 100 ml volumetric flask, which was attached to the pump by the rubber tube, and from the other side of the pump was joined with the column. While the other parameters were kept constant, including the mass of Mnt/sand backed in the column (3 g), flow rate (10ml/min), height of column (8 cm), and Temperature at 25 ◦C. After setting the pump on the reported value, the solution would flow from the flask, passing through the Mnt/sand column and exiting out from the bottom hole, making it easy to collect in a urine cup and immediately measuring the final concentration by UV-vis spectrometer. The used Mnt/sand column was regenerated by thermal decomposition, which will be used in subsequent experiments.

2.7.2.3 Effect of Flow Rate

As a critical factor in the continuous adsorption technique, the flow rate was investigated at five values: 2, 4, 6, 8, and 10 ml/min. Other parameters were kept constant, involving the concentration of PHY solution (50 ppm, 100 ml), at 25 ◦C. After preparing the five working solutions, each was applied at a different flow rate by setting the pump at the needed rate. Accordingly, each run will consume a different time. At the end of each run, the treated solution was collected and directly analyzed by the UV-vis spectrometer.

2.7.2.4 Effect of Temperature

Adsorption temperature affects the adsorption mechanism, whether in the batch or column system, so it was examined in this study at 20, 30, 40, and 50 ◦C. Adjusting the temperature in the column system was performed by the Julabo bath/circulation thermostat (CORIO), in which the solution container was immersed until thermal equilibrium was reached, then the continuous adsorption was run under the thermostat. Maintaining other parameters constant, with PHY initial concentration (50ppm), flow rate (10 ml/min), and mass of column padding (6 g), the hole experiments were applied on the same column with thermal regeneration before each run. The percentage of removal can be calculated from the initial and final concentration of the treated PHY solutions measured by the UV-vis spectrophotometer.

2.7.2.5 Effect of the column Height

A comparison between two different columns' heights (diameters) in this study was made, maintaining the mass of the backed Mnt/sand adsorbent constant. Two columns of 7 and 10 mm measured diameters were backed with 3 g of Mnt/sand, resulting in 8 and 4 cm column heights, respectively. For each column, 100 ml of 50 ppm PHY solution was pumped through it under constant conditions. By UV-vis spectrophotometer measurements adsorption efficiency can be computed and compared.

2.7.2.6 Column Reusing

The reusing procedure in the column system is more easily handled than the batch system, as reported in this work. The Thermal decomposition technique was applied to recover and reuse the adsorbent. In addition, the adsorbent material (Mnt/sand) was tightly packed in the column between two layers of glass wool, which made it stable when the column was disjointed from the setup of work. After the continuous adsorption run had been over which applied with 6 g backed column, 8 cm column height, pumping 200 ml of 50 ppm PHY solution, at flow rate 10 ml/min at room temperature, the Mnt/sand column was disjointed and transferred into the furnace at 550 ◦C for 2 h (as adjusted). Then, it is taken out from the furnace to cool before it is reused in the upcoming experiments. For the column, it was reused six times, and the efficiency was calculated for each experiment.

2.7.2.7 Effect of Thermal Decomposition Temperature

With regard to energy saving, a brief study has been done on the temperature of the thermal decomposition process, which is used in this work as a recovery technique for contaminated Mnt/sand to reuse multiple times. According to the TGA result of PHY in previous studies, it completely decomposed at 650 ˚C, so it is supposed to set the furnace at this temperature to do thermal decomposition. In this study, thermal decomposition was applied at lower temperatures for the same Mnt/sand column, specifically at 600, 550, 500, 450, and 350 ◦C, after every run. The experiment run repeated for each temperature of thermolysis, and it was done with 50 ppm PHY solution, the temperature of the solution (25 ◦C), flow rate (10 ml/min), mass of backed Mnt/sand in the column (6g), height of column (8 cm) for 2h. After each different temperature thermal decomposition, the adsorption efficiency of the treaded column can be calculated by measuring the influent and effluent concentration of the PHY by UV-vis spectrophotometer.

2.7.2.8 Computational Study on PHY Adsorption on Montmorillonite

A computational analysis was used in this work to examine the effects of PHY adsorption onto the Mnt surface, with respect to the changes in bond length and adsorption energy, in order to look into energy conservation. Since the bond length indicates the strength of the bond, it can be linked to the energy needed to break it, especially during the thermal regeneration process (decomposition process).

2.7.2.9 Adsorption of Phenazopyridine in Continuous System

(Time Dependency)

The influent PHY solution with a concentration of 50 ppm was pumped with a flow rate (2 ml/min) through a column baked with 3.0 g of Mnt/sand was investigated. The PHY effluent was sampled at regular 3 minutes for around 1.5 h using a 200 ml working solution.

To demonstrate the effectiveness of the adsorbent in the fixed-bed column, breakthrough curves were employed in an unconventional manner [79] . For a given condition, the breakthrough curve is expressed as a function of time in terms of C_t/C_0, where C_t is the influent concentration and C_0 is the effluent concentration [93]. The breakthrough curve could be used to determine the adsorbent's adsorption capacity under specific operating conditions.

The point at which the effluent concentration (C_t) approaches 10% of the influent concentration (C_0) is known as the breakthrough point. Breakthrough time (t_b) is the corresponding time. Exhaustion point and exhaustion time (t_e) are reached when the effluent concentration reaches 95% of the influent concentration [93].

2.8 Characterization of Solid Materials

2.8.1 FT-IR Characterization

Fourier transmission infrared radiation spectrophotometer (FT-IR) was used to identify the surface functional groups on Mnt/sand as a pure sample; in addition, pure PHY was also analyzed. After the adsorption process was done, a contaminated Mnt/sand was also analyzed in order to prove the existence of adsorbed PHY on the surface of Mnt/sand. Subsequently, the thermally regenerated sample of the contaminated Mnt/sand was analyzed to confirm the absence of any organic leavings at the adsorbent surface that related to PHY, which would ensure that complete decomposition had taken place.

2.8.2 X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM)

Characterization of Mnt/sand and pure Mnt was done using scanning electron microscopy (SEM), which provides an observable indication of the Mnt/sand particle structure and shape at the micro level. In addition, X-ray diffraction (XRD) analysis was performed to estimate the crystalline/amorphous nature of adsorbent materials (Mnt/sand and pure Mnt), which helps in understanding their composition and properties. In general, these techniques propose a powerful way to characterize materials and give insight into material crystallographic and microstructure properties.

2.8.3 Thermogravimetric Analysis (TGA)

The thermal stability of Mnt/sand was assessed through thermogravimetric analysis (TGA) by observing the loss of its mass as a function of heating temperature. Moreover, it helps in determining the range of temperature where the material stays stable, which was the aim of the application on the adsorbent material (Mnt/sand). Also, TGA places potential degradation temperature points for the material, as it was with the PHY sample, to determine at which temperature it would completely decompose, to be approved in regeneration experiments.

Chapter Three

Results

3.1 Characterization result of Adsorbent and Adsorbate

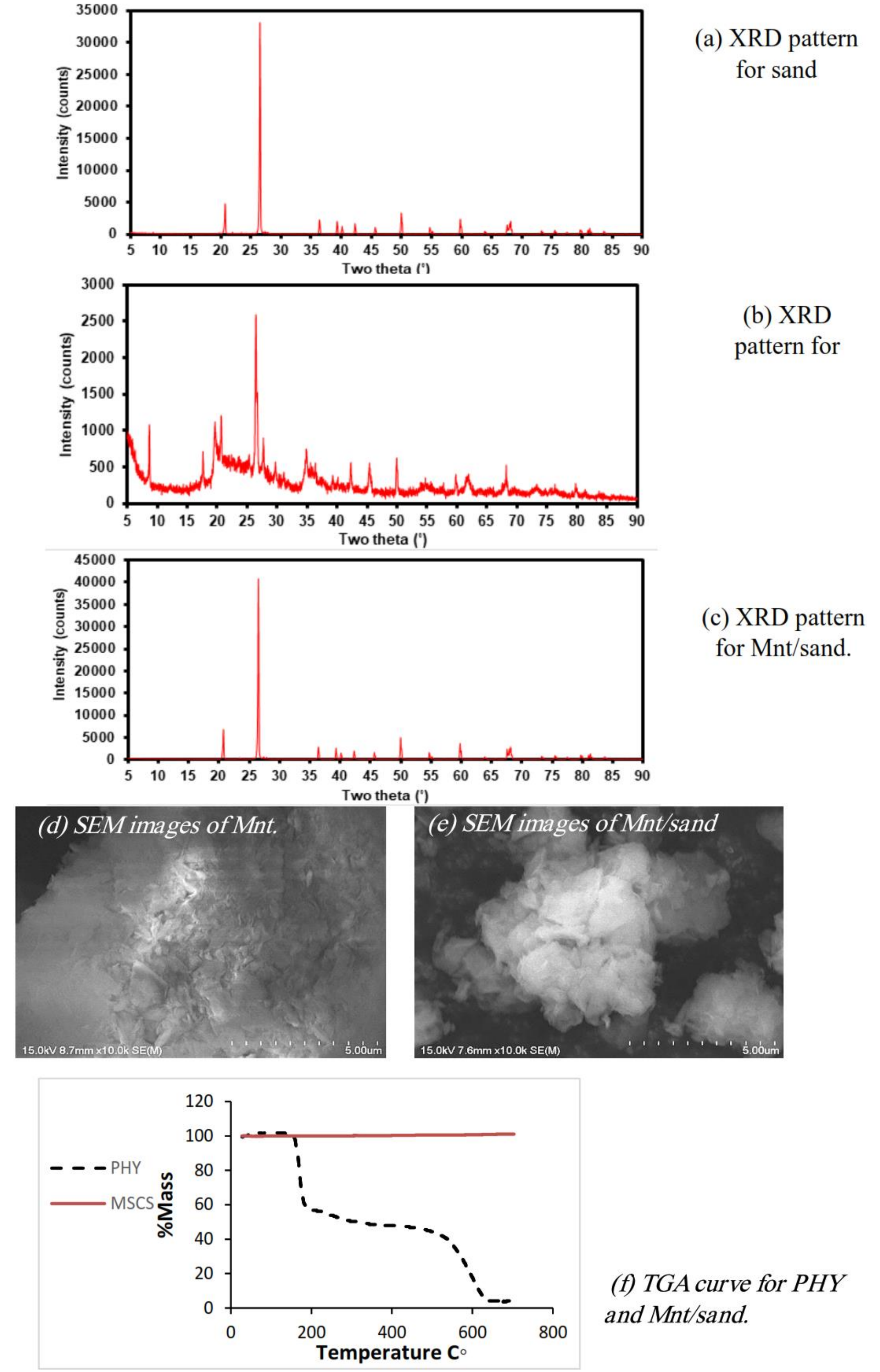
The X-ray diffraction (XRD) analysis was used for sand, Mnt, and the synthesized adsorbent Mnt/sand. Each material produced unique patterns, as shown in Figure 3.1. The XRD patterns are related to sand minerals, the main reflections corresponding to 20.68°, 26.48°, 36.36°, 39.32°, 50.02°, and 68.18° with intensities of 4850, 33158, 2312, 1862, 1754, 2775 and 2100. For Mnt clay, the main patterns are at angles of 8.74°, 20.68°, 26.48°, 34.92°, 49.92°, and 68.16° with their related intensities of 1020, 1191,2566, 716, 629, and 529. The composite of synthesized from both produced an integrated spectrum and showed the reflections related to both materials at angels 20.68°, 26.48°, 36.36°, 39.3°, 50.02° and 68.18° with intensity of 5912, 40712, 2425, 2579, 3554, 2604.

Crystalline structure of the minerals involved in the adsorbent composite can be confirmed by the XRD analysis, offering a strong indication of Mnt/sand mineralogical composition. In addition, the well distinct and sharp peaks that were detected indicate a high degree of crystallinity, which is vital for the adsorption characteristics of the Mnt/sand. If we follow the highest pattern at 26 (2Θ) its common between sand and Mnt, associating with the crystalline SO_2 structures exists in both, for the sand it has intensity 33158, and for Mnt 2566, but for the composite it appeared with 40712, indicates kind of combination between both materials, and its kind of physical blending, no chemical interaction occurs, because the sand introduced as supporting material (core) for Mnt (shell). Other Mnt patterns have intensity ranged between (500-1000), shown in Fig.3.1.a, are not clearly detectable in composite spectra Fig.3.1.c, relative to very high intensity of sand pattern, reach intensity of 40000.

The SEM images provide an extensive examination of the Mnt/sand, offering valuable information about their size, shape, composition, morphology, and crystal structure. SEM analysis thus revealed that pure Mnt has a fine particle structure; therefore, there are no agglomerated fragments or voids through it, as Fig. 3.1. d shows.

Figure 3.1

Characterization results



(a) XRD pattern for sand

(b) XRD pattern for

(c) XRD pattern for Mnt/sand.

(d) SEM images of Mnt.

(e) SEM images of Mnt/sand

(f) TGA curve for PHY and Mnt/sand.

On the other hand SEM image for the granular crystals of the montmorillonite/sand composite (Mnt/sand), shown in Fig 3.1.e exposed distinct composite structures, aggregating into a layered, cloudy porous texture (Figure 3.1.e). The surface area of the layered configuration is significantly increased, improving the adsorption capacity and efficient interaction with contaminants. More significantly, the porous structure facilitates easy pollutant migration in the interlayer spaces by creating holes and cracks. Thus, optimal contact between contaminants and adsorbents greatly increases Mnt/sand's overall adsorption capacity. Mnt/sand is a promising agent for use as a potential and efficient adsorbent of pollutants, as demonstrated by all these structural characteristics. For further analysis, A7 showed the elemental composition of the Mnt and Mnt/sand, which are mainly composed of silicon, oxygen, and other elements.

A critical characterization technique in this work is Thermogravimetric Analysis (TGA), which offers an indication of thermal stability and determines the decomposition temperature for the materials. Fig.3.1.f shows the TGA results of Mnt/sand, which displayed no significant loss of mass as it was heated, confirming the high thermal stability of this adsorbent up to 700 ◦C, which ensures the suitability for hard condition environmental applications as a durable and sustainable adsorbent material in adsorption-thermolysis technique. On the other hand, the TGA result of PHY shows a complete loss of the PHY sample, which can be divided into three periods below 650 ◦C, the most significant loss of mass (45%) happened approximately between 160-210 ◦C, that can be related to the azo group N=N bond breaking down. The second period ranged between 210-500 ◦C with a mass loss of 10%, and the last one continued to 650 ◦C, ending with complete decomposition of the PHY sample, this temperature is related to the decomposition temperature for PHY.

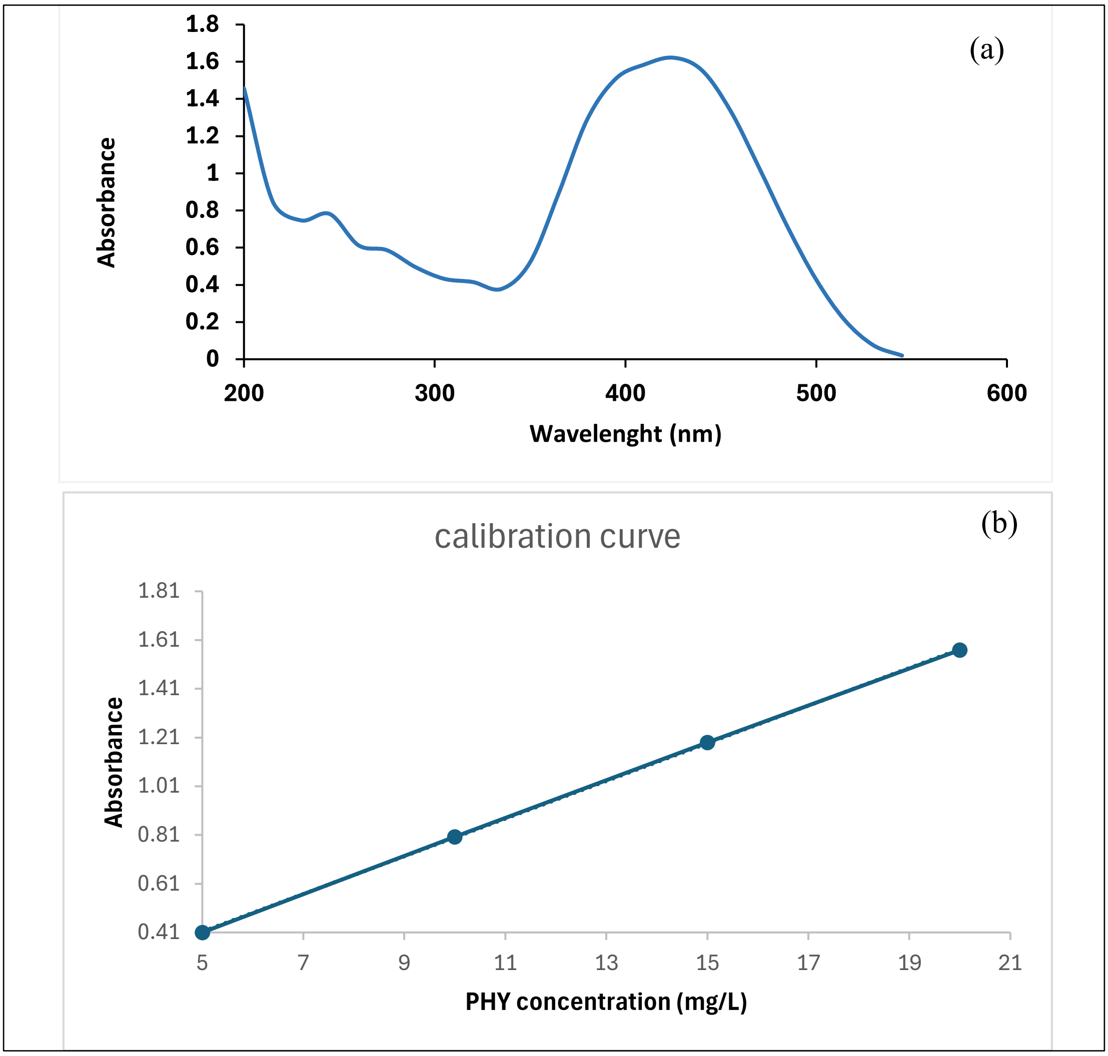
3.2 Calibration Graph of PHY

UV-VIS spectrophotometry was used favorably over other analysis methods due to its suitability, ease, speed, and minimal pollution effects. In addition, it gives the ability to investigate the progress of the adsorption process by measuring the change in PHY concentration during the adsorption process at regular time intervals.

The absorbance spectrum of PHY solutions was measured at the maximum absorbance wavelength (λ_{max}), and it was obtained that the maximum absorbance wavelength (λ_{max}) = 425 nm for a 20 ppm PHY solution, as shown in Fig.3.1.

Figure 3.2

Absorbance Spectrum and calibration curve of Phenazopyridine



Note: (a) Absorbance Spectrum of Phenazopyridine. (b) A typical calibration curve for PHY by UV-VIS spectrometric method**.**

A model calibration curve of 5, 10, 15, and 20 ppm PHY solutions measured at λ_{max} = 425 nm is shown in Fig.3.2. (b) Which is used in PHY concentration analysis. According to the calibration curve, the correlation coefficient (R^2) =0.999, which indicates a linearity of this calibration curve. The limit of detection (LOD) and limit of quantification (LOQ) were calculated considering the slope (S) and standard deviation (σ) of the response using the following equations[94]:

$$\mathrm{LOD} = \frac{3.3\sigma}{S} \text{ ………………..(3.1)}$$

$$\mathrm{LOQ} = \frac{10\sigma}{S} \text{ ………………...(3.2)}$$

And they were found to be 0.25, 0.78 respectively, and the molar absorptivity from the slope was 0.07 L $\mathrm{mol^{-1}\ cm^{-1}}$.

3.3 Adsorption of PHY

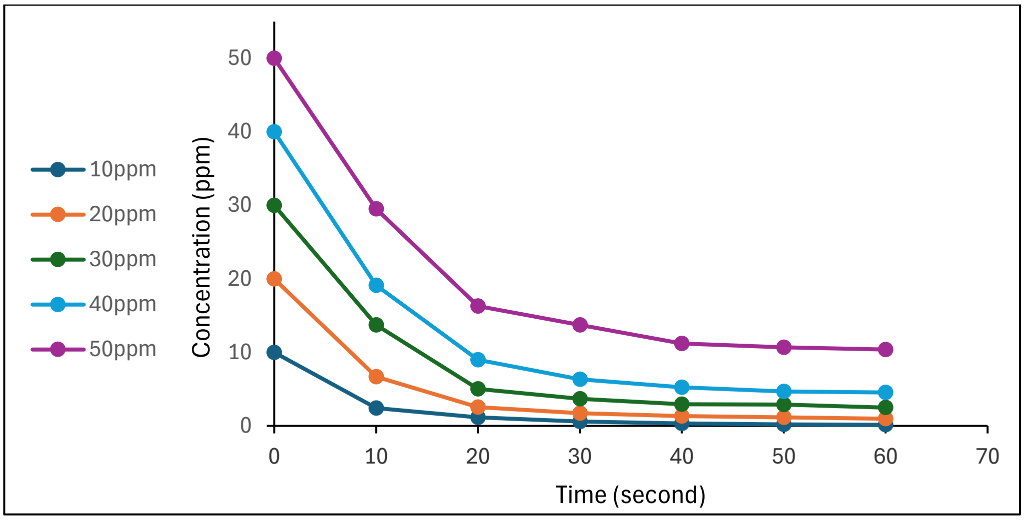
3.3.1 Adsorption of PHY in Batch System

3.3.1.1 Effect of Initial Concentration (Time Dependency)

A range of initial concentrations (10, 20, 30, 40, and 50 ppm) of the PHY standard solutions were adsorbed onto 0.5 ± 0.01 g of Mnt/sand, Figure 3.3 shows how the concentrations drop over time.

Figure 3.3

Concentration of phenazopyridine lasting vs contact time with Mnt/sand



According to the results, the concentration of PHY in the solution quickly decreased in the first 20 minutes, as seen in Fig. 3.3, indicating that adsorption occurred rapidly during this period. The adsorption of PHY continued for another 40 minutes, and as the data showed, the equilibrium would inevitably be reached within 60 minutes, achieving maximum adsorption. For all adsorption batch experiments, 1 hour was established as the marked contact time, ensuring constant conditions for equilibrium in the subsequent studies.

The quick initial adsorption of PHY is a surface phenomenon that occurred because of the empty holes Mnt/sand particles have, which rapidly filled up in the first period, that's followed by a nonsignificant variation after equilibrium is reached. In which PHY molecules undergo a gradual migration and diffusion, and the rate of adsorption sharply drops to reach the equilibrium or the steady state. In the first 20 minutes, 92-86% of PHY was adsorbed from the total percentage of removal for initial concentrations ranging between 10-50 ppm, respectively.

Table 3.1

The percent of removal for each initial concentration

Initial concentration (ppm)	C_1 10	C_2 20	C_3 30	C_4 40	C_5 50
% Removal	99%	96%	93%	89%	80%

Another way to look at the impact of PHY's initial concentration is to say that the lower the adsorption efficiency, the higher the initial concentration, as shown in Table 3.1.

These results are explained by the surface phenomena that control the adsorption mechanism, when the concentration is low there are plenty of adsorption sites for adsorbent molecules, causing a high percent of removal, in contrast, high concentrations impose the adsorbate molecules compete on those available sites, by and by all free sites become occupied, when they are completely saturated adsorbent reached a point with no further significant adsorption despite any increasing in PHY concentration. Which then decreases the efficiency of adsorbate removal.

3.3.1.2 Adsorption Isotherms

Studying adsorption isotherms is important in constructing an adsorption system. They provide insight into adsorbent surface properties, adsorption mechanism, and the measurement of the adsorption capacity for the used adsorbent. As exhibited in Table 3.2, equilibrium concentrations of different initial PHY concentrations and masses adsorbed onto Mnt/sand were computed.

Table 3.2

Equilibrium concentrations and masses adsorbed for PHY onto Mnt/sand.

C	Ce	qe	1/C	1/qe	Log Ce	Log qe
10	0.98	1.98	1.01	0.50	0.01	0.29
20	2.35	3.69	0.42	0.27	0.37	0.56
30	4.81	5.62	0.20	0.17	0.68	0.75
40	8.80	6.18	0.11	0.16	0.94	0.79
50	16.12	7.05	0.06	0.14	1.20	0.84

In this study, the relationship between the mass of PHY adsorbed and its concentration at equilibrium in the solution at 30 °C was described using the Langmuir and Freundlich isotherm models.

As seen in (Figure A.13.b), the Langmuir isotherm was determined from the relationship between 1/qe vs. 1/Ce, according to equation 3.1:

$$\frac{1}{q_e} = \frac{1}{K_L\, q_{max}} . \frac{1}{C_e} + \frac{1}{q_{max}} \qquad (3.3)$$

Where:

C_e = Adsorbate concentration at equilibrium (mg/L).

q_e = Adsorbent amount that adsorbs per unit mass of adsorbent at equilibrium(mg/g).

q_{max} = Maximum adsorption capacity constant at equilibrium (mg/g).

K_L = Langmuir adsorption equilibrium constant (L/mg).

The relationship between Log qe and Log Ce, as shown in (Figure A.13.c), provided the Freundlich isotherm, depending on the following equation:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \qquad (3.4)$$

Where:

C_e = Adsorbate concentration at equilibrium (mg/L)

q_e = Adsorbent amount that adsorbs per unit mass of adsorbent at equilibrium(mg/g).

K_F = Freundlich constant indicates adsorption capacity.

n = Empirical constant.

Employing the linearized form of the Langmuir and Freundlich equations, the parameters of the adsorption isotherm were obtained from the intercept and slope of the linear plots. The adsorption followed the Langmuir isotherm more closely than the Freundlich isotherm because the Langmuir isotherm's R^2 is closer to the unit, taking the value of 0.996, as Table 3.3 shows, which indicates a homogeneous surface of the adsorbent with the same adsorption energy for all adsorption sites, and a single layer of adsorbed molecules is formed (monolayer adsorption).

The maximum adsorption capacity (q_{max}), or monolayer adsorption capacity, was found to be 8.98 mg/g based on the Langmuir plot of $1/q_e$ versus $1/C_e$ (Figure A.13.b). Adsorption-desorption equilibrium constant (K_L), which was determined to be 0.29 L/mg, as Table 3.3 shows, assigns a higher adsorption capacity at higher concentrations. These results underline the high affinity of adsorption of Mnt/sand for PHY caused by monolayer adsorption on a homogeneous surface, assisting it to function effectively as an adsorbent in water purification applications.

The Freundlich adsorption isotherm constants affect the adsorption intensity and capacity. Typically, when the K_f value rises, the adsorbent's adsorption capacity consequently rises. Freundlich isotherm $K_f = 2.30$ (mg/g) indicates a high adsorption capacity can be related to the large surface area of Mnt and strong electrostatic attraction between Mnt/sand and PHY. When the value of n falls between 1 and 10, the adsorption process is considered advantageous [95]. As this implies, PHY adsorption on Mnt/sand applied in this work is valuable, with the (n) value of 2.21. Table 3.3 shows the Langmuir and Freundlich isotherm model parameters for the PHY adsorption onto the prepared Mnt/sand in this work.

Table 3.3

The parameters of Langmuir and Freundlich isotherm models

Isotherm	Langmuir			Freundlich		
parameter	q_{max}(mg/g)	K_L(L/mg)	R^2	K_f ((mg/g) (L/mg))$^{1/n}$	n	R^2
value	8.98	0.29	0.99	2.30	2.21	0.92

3.3.1.3 Adsorption Thermodynamics

The following formulas can be used to calculate the thermodynamic parameters of adsorption, such as changes in the standard free energy (ΔG°), standard enthalpy (ΔH°), and standard entropy (ΔS°) [95, 96].

$$\text{Ln}\, Kd = (\Delta S\ \circ)/R - (\Delta H\ \circ)/RT \qquad (3.5)$$

With T (K) representing the absolute solution temperature, R (8.314 J/mol K) being the universal gas constant, and K_d expressing the distribution coefficient, which can be determined as follows:

$$K_d = CAe/Ce \qquad (3.6)$$

Ce (mg/L) is the concentration at equilibrium, and C_{Ae} (mg/L) refers to the amount adsorbed on the solid at equilibrium. For the value of ΔG°, the following relation can be used:

$$\Delta G = -RT\, lnK_d \qquad (3.7)$$

$$\Delta G = \Delta H - T\Delta S \qquad (3.8)$$

Figure A.14 shows the slope and intercept of the linear variance ln K_d with relevant temperature (1/T), which are used to derive the values of ΔH° and ΔS°, respectively.

The experiments in this study were done at different temperatures ranging from 10 to 50 °C. The thermodynamic values that were obtained are listed in Table 3.4

Table 3.4

Thermodynamic parameters of PHY adsorption on Mnt/sand

Parameter	ΔG° (KJ/mol)					ΔH° (KJ/mol)	ΔS° (J/mol. K)
Value	283 °C	293 °C	303 °C	313 °C	323 °C	18.253	55.784
	-0.733	-2.463	-3.192	-3.680	-3.444		

The endothermic adsorption was proved by the positive values of ΔH°=18.253 from Van't Hoff equation, as shown in Table 3.4, in other words, the adsorption capacity of Mnt/sand increases as the temperature of PHY solution increases, while the spontaneous adsorption process on Mnt/sand was indicated by the negative values of ΔG° at various temperatures, while the more negative value of ΔG° at higher temperatures indicate a favorable adsorption under higher temperature conditions, that confirms with the observation that it is endothermic overall process. Moreover, this is in agreement with equation 3.4, which requires high temperatures when the values of ΔH° and ΔS° are positive, in order to have spontaneous adsorption. The positive value of ΔS° indicates an entropically favorable adsorption process. Entropy rises as a result of the water molecules that were bonding with the adsorbate becoming free due to the adsorbed species.

3.3.1.4 Adsorption Kinetics

Adsorption kinetics study is important for wastewater treatment. It provides insight into the mechanism of this adsorption process and important information about the reaction pathways. Furthermore, the adsorbate uptake rate, which controls the residence time of adsorbate at the solid–solution interface, is described by kinetics. Estimating the rate at which pollutant is adsorbed from aqueous solutions is therefore crucial for designing suitable sorption systems [97].

Dynamical experimental data were analyzed using the pseudo-first-order kinetics model, the pseudo-second-order kinetics model, and the intraparticle diffusion model. Based on the pseudo-first-order kinetic model, the rate of adsorption is thought to be proportional to the difference between the amount adsorbed at any given time and the saturation concentration. In contrast, the pseudo-second-order model more accurately represents the adsorption behavior over the whole time interval and assumes that chemisorption is the rate-controlling step. Information regarding material movement within the boundary layer and pores during the adsorption process is provided by the intraparticle diffusion model.

Lagergren introduced the pseudo-first-order model by the equation [98]:

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \qquad (3.9)$$

In which k_1 is the rate constant (min^{-1}), and the amounts of adsorbate (mg/g) adsorbed on the clay at equilibrium and time t are represented by q_e and qt, respectively.

The linear plot of log (q_e-q_t) against t, as shown in Figure A.10.a has a slope and intercept that were used to determine the kinetics parameters (K_1 and q_e). That data was summarized in Table 3.5.

Additionally, the sorption data was examined using a pseudo-second-order mechanism(101), which was explained by:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (3.10)$$

Where k_2 is the pseudo-second-order sorption rate constant (g/mg.min). The plot of t/q_t against t in Eq. (8) should provide a linear relationship if second-order kinetic is applicable, from which the constants q_e and k_2 can be found from the slope and intercept as Figure A.10.b shown.

Table 3.5 also provides the values of constants q_e and k_2 for pseudo-second-order sorption. Using the intraparticle diffusion approach presented by Weber and Morris, adsorption systems where intraparticle diffusion may be the rate-limiting step are employed. Using the Weber and Morris equation, the rate constants for intraparticle diffusion (ki) are calculated [99]. This equation's description is:

$$q_t = k_i t^{0.5} + c \qquad (3.11)$$

Where k**i** and c are the intraparticle diffusion rate constants (mg/g.min$^{1/2}$).

Table 3.5

Parameters of pseudo-first-order model, pseudo-second-order model, and intra-particle diffusion model

The model	Pseudo-first order Kinetic model			Pseudo-second order Kinetic model			Intra-particle diffusion kinetic model		
Parameters of the model	K_1 (min^{-1})	qe (mg/g)	R^2	K_2 (g/mg.min)	qe (mg/g)	R^2	K_p (mg/g.min$^{1/2}$)	A	R^2
Values	0.089	1.139	0.946	0.347	2.191	0.997	0.3	0.359	0.844

According to the previous plots, and parameters values shown in Table 3.5, the pseudo-second order kinetics model's calculated correlation coefficient (R^2=0.997) is nearer unity than the pseudo-first order (R^2=0.946), and intra-particle kinetics models (R^2=0.844), which has low value suggests that intra-particle diffusion kinetic model is not the rate limiting step. The adsorption process can be characterized with q_e=2.191 (mg/g) and K_2 = 0.347 (g.mg^{-1}.min^{-1}) based on pseudo-second order kinetics. This model suggests that chemisorption is the rate-limiting step in the adsorption process, which can be readily proved by a monolayer or multilayer adsorption [100], and as previously discussed in adsorption isotherms, monolayer adsorption is obtained which confirms with kinetics results. On top of that, it is observed that the calculated value of q_e (2.191) for the Mnt/sand based on the pseudo-second-order model and the experimental value of q_e (2.174 mg/g) agree well.

Determining the activation energy (Ea) value of the adsorption mechanism is a vital parameter, which enables the prediction of how temperature can affect the rate of reaction by providing insights into the response mechanism. The data collected in temperature effect experiments are used in activation energy calculations, which were applied to the Arrhenius equation [97], which is represented by the following formula:

$$k = Ae^{-Ea/RT} \qquad (3.11)$$

The following equation is a representation illustrating how the Arrhenius equation could be transformed into its linear form:

$$ln\, k = \frac{-Ea}{RT} + lnA \qquad (3.12)$$

Where K expresses the rate constant, A is the Arrhenius constant (pre-exponential factor), R is the ideal gas constant (8.314 J/mol.K), and T is the temperature in kelvin. First, measure the rate constant from (Ct-Ci)/Δ t, where Ct and Ci are the time t and initial concentration of PHY solution, and Δ t is the period of time. Then, from the plot of lnK vs 1/T, as shown in Figure A.10.(d), the value of Ea and K can be calculated through the slope and intercept, respectively.

The value of Ea can give insight into the nature of the adsorption process and the tendency of being physisorption or chemisorption. Physisorption usually has a near-zero value of Ea (0-40 kJ/mol), however, chemisorption has a much stronger interaction, meaning a large value of Ea, which can be activated chemisorption or non-activated (less frequently)[101]. Activated mechanism countered to a high Ea means an extreme variation of rate with temperature. While in some cases adsorption occurs very fast, suggesting a small activation energy, which is specified as a non-activated chemisorption [101]. As obtained in this study from the Arrhenius plot, Ea has a value of 30.4 kJ/mol. Determining the effective mechanism of PHY adsorption on Mnt/sand depends not only on the Ea value. Considering previous models, and the relatively small Ea, this adsorption can be a mixture of physical and chemical.

3.3.1.5 Effect of pH

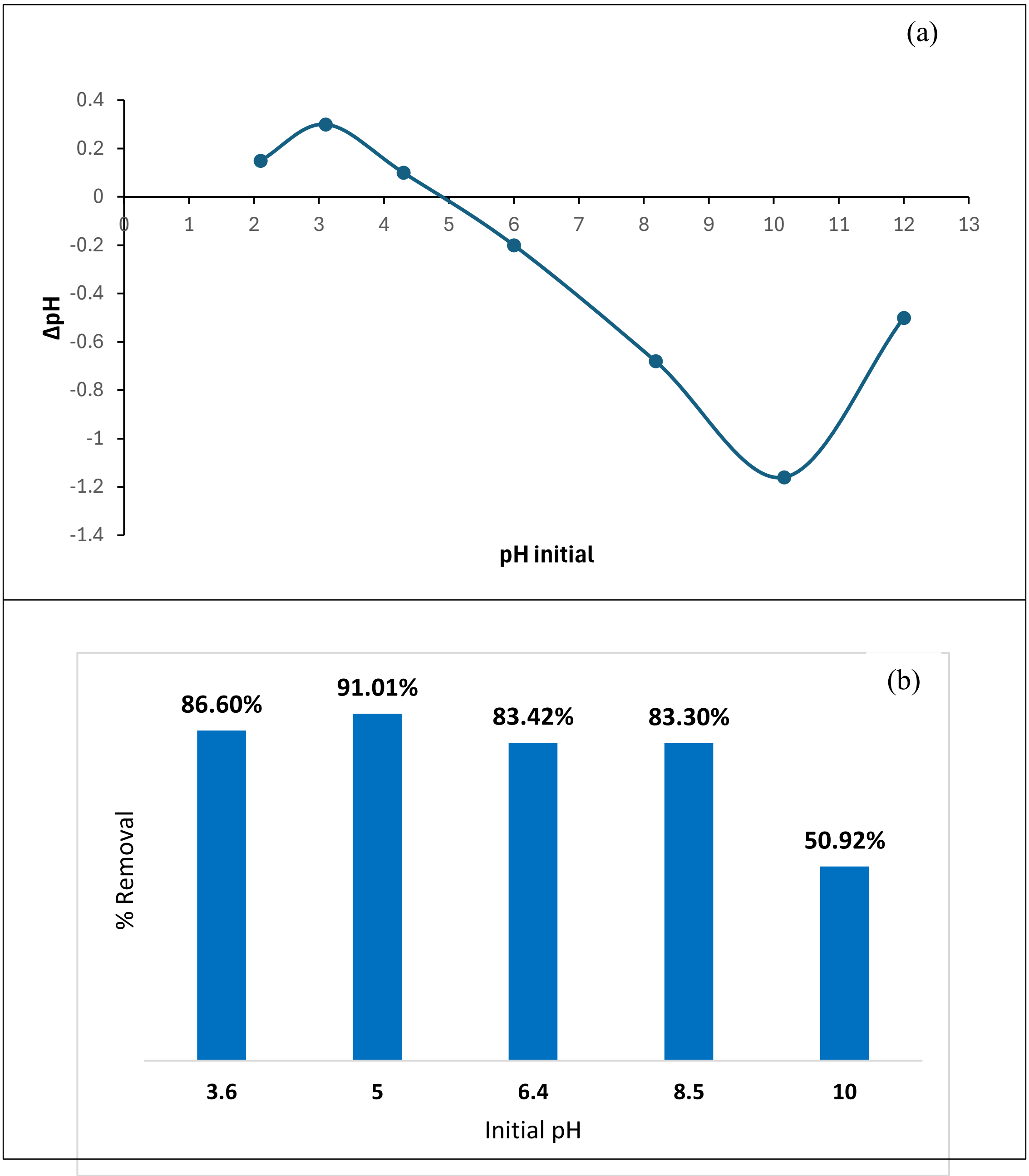
From the point of zero charge experiment, results showed that at pH of 4.8, the Mnt/sand has no charge, which means that the negative charges at the adsorbent surface are electrostatically neutralized with positive H+. This pH is called the point of zero charge (PZC), which can be determined by the intercept of the plot of the ΔpH vs. the initial pH of the mixture of Mnt/sand and the 0.1 M KCl, as shown in Fig.3.4.(a). At pH values below 4.8, the adsorbent surface displays positively charged low adsorption, and as pH rises, the adsorbent surface becomes negatively charged, and adsorption decreases.

The change in PHY adsorption onto clay was examined as a function of the initial solution pH. The data are shown in Fig3.4.(b) The pH of the solution, which impacts the topography of the sorbent and adsorbate structure as well as surface characteristics, significantly affects the adsorption of PHY from an aqueous solution onto the surface of Mnt/sand.

Depending on how the clay's surface chemistry and structure properties changed, the adsorptive behaviors can be understood for the clay, both below and above pH_{PZC}. In addition pKa of PHY equals 5.2 (as weak base drug), determines how it behaves at different pH, plays critical role in adsorption performance[102].

Figure 3.4

Effect of pH



Note: (a) Plot of delta pH versus initial pH The results were obtained at room temperature. (b) Effect of initial pH of solution on %Removal of PHY onto Mnt/sand.

The best adsorption achieved in the acidic medium, especially at pH (5) as shown in Fig.3.4.(b) where the Mnt/sand has a negative charge (above pH_{PZC}), and surely PHY has positive charge in the protonated form (bellow pKa), since this high adsorption efficiency can be related to the PHY cations' attraction for negatively charged active sites in Mnt in the post-PZC acidity region. Another reason can be referred to as the oxides of clay surface have been removed, so increased accessibility of protonated PHY molecules interlayer regions.

For neutral medium pH around (6.5), PHY molecules almost in neutral form still attract to negatively charged Mnt giving respectable adsorption performance, until reaching very basic environment pH(10) were hydroxide ions totally neutralize hydrogen ions to the point where the solution becomes basic, acquiring a negative charge surrounding PHY, this eventually repulsed negative Mnt/sand away, which explains the noticeable decrease in adsorption capacity in the basic region.

On the other hand, when the pH values drop to pH 3.6, we expect the Mnt/sand to have a positive charge (below $\mathrm{pH}_{\mathrm{PZC}}$), which means repulsion with the more positive PHY ions, and thus the adsorption capacity decreases slightly in this region, but still show notable adsorption, that can be due to other physical attraction as trapping.

These results approve that PHY adsorption is optimized at pH 5, which is comparable to the initial pH of the PHY solution.

3.3.1.6 Effect of Amount of Adsorbent

Figure A.11 shows the results of calculating the amount of PHY adsorbed on Mnt/sand (q_e) and the percentage removal versus different amounts of Mnt/sand. According to Figure A.11.a, the percentage of PHY removed rises as the amount of Mnt/sand adsorbent increases. This is because there are more adsorption sites and a larger surface area.

As the amount of Mnt/sand increases, Mnt/sand capacity decreases, as shown in Figure A.11.b. This is because the adsorbent's sites become saturated with the limited concentration of PHY even with increasing the dosage of Mnt/sand, which reduces the ratio of surface area that PHY can occupy, minimizing the adsorbent efficiency. Furthermore, the adsorbent amount affects the rate of adsorption, such that the larger Mnt/sand amount, the faster adsorption occurs. These findings ensure that 0.5 g is the optimal dose, whereas any additional increase just speeds up the adsorption rate without further significant efficiency.

3.3.1.7 Regeneration and Reusing of Mnt/sand by Thermolysis

3.3.1.7.a FT-IR Results

Adsorption experiments using UV-visible adsorption spectroscopy demonstrated the adsorption of PHY onto Mnt. The spectroscopy was used to observe the decrease in PHY concentration over time until equilibrium was reached. The results were previously discussed. Furthermore, by performing FT-IR analysis on a crashed dry sample of Mnt/sand that has come into contact with a PHY solution, the results can offer a crucial indication of the interaction between PHY and Mnt.

Figure 3.5. (a) presents the FT-IR spectrum of fresh Mnt/sand. The Si–O stretching vibrations related to the strong band at 1050 cm^{-1} point out that the Mnt surfaces contain a significant number of silanol (Si-OH) groups, Also, it can be related to Si–O stretching and bending of silica component SO_2. Spectrum also shows small, broad bands at 3618 cm^{-1} and 3448 cm, which can be attributed to the –OH stretching vibration of the Mnt's structural hydroxyl groups and any water molecules adsorbed in the interlayer during measurement and sampling. It is also possible to attribute the bands at 650 cm^{-1} and 620 cm^{-1} to Si–O–Al and Si–O–Mg, respectively [103].At 804 cm^{-1}, the band can be related to quartz [104].

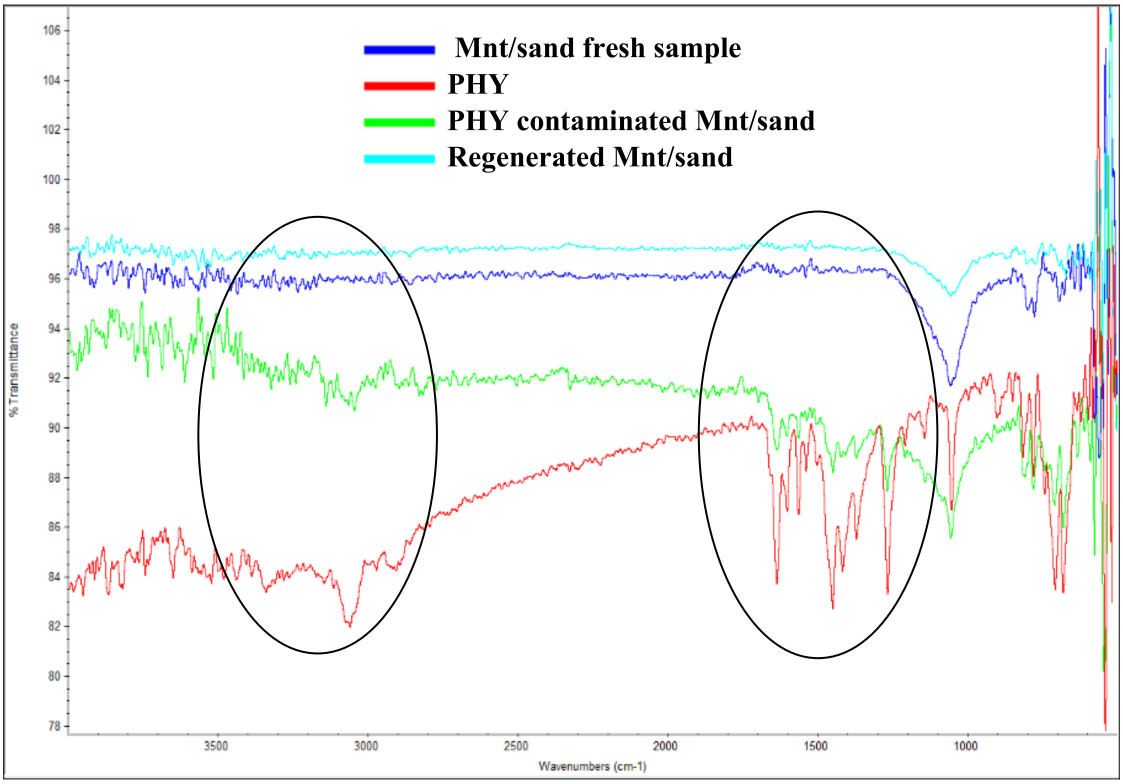
The FT-IR spectrum of PHY is shown in Fig. 3.5. (b), displaying adsorption peaks, such as the N-H stretching vibration at 3519.54, 3436.44 cm, and 3334.88, in addition to bending vibration occurring at 1635. Aromatic C-H stretching at 3060.41, and the peak at 2900. 18 cm^{-1} C-H aliphatic. C–H bending at 1458, and 1639.14 cm^{-1}. For the azo group (N=N) stretching vibration, the band at 1449.43 cm^{-1} can be linked to it, and the one for C-N in aromatic amine occurs at 1449 cm^{-1}, and for C=N stretching at 1601 cm^{-1} (105).

Fig.3.5(c) displays the FT-IR spectrum of Mnt/sand adsorbed the PHY. It shows the strong bands at 1639.14 cm^{-1} and 1449 cm^{-1} that are attributed to PHY, besides the other peaks related to PHY appear in the regions of 1200-1640 cm^{-1}, and the main strong band at 1050 cm^{-1} that is attributed to Mnt. The presence of adsorbed PHY on the Mnt/sand surface is confirmed by these findings.

The regeneration of PHY-contaminated Mnt/sand by thermolysis was applied in this work for the first time. Depending on the TGA analysis of the PHY sample, which shows complete thermolysis of pure PHY at 650◦C, as presented in Figure 3.1.(f), thermolysis was applied to the contaminated Mnt/sand at 650◦C after each run of adsorption. The FT-IR spectrum of the regenerated Mnt/sand is represented in Fig.3.5, which shows the loss of all peaks related to PHY. This asserts that the adsorbed PHY undergoes thermal degradation, which means full removal of PHY from Mnt/sand by the thermolysis process. Moreover, the FT-IR spectrum of treated Mnt/sand and the first use of Mnt/sand can be compared, exhibiting a similar spectrum with identical peaks.

Figure 3.5

FT-IR spectra of Mnt/sand, PHY, PHY contaminated Mnt/sand, regenerated Mnt/sand



3.3.1.7.b Reusing Experiments

Figure A.12 Reports that regenerated Mnt/sand can be reused several times repeatedly without incurring a noticeable reduction in its adsorption efficiency. The experiment of 0.5 g of Mnt/sand with 20 ppm PHY solution, volume of 100 mL, at room temperature, for 1 h of shaking, has been done 5 times in sequence, and Figure A.12 reports the percentage of PHY removal for each, ranging between 94-85%. This established that the regenerated Mnt/sand has no significant failure in its adsorption efficiency.

3.3.2 Adsorption of PHY in Continuous Flow System

Even though the batch system is a quick and effective method for water purification on a small scale, it typically includes mixing, centrifuging, and separating steps, which are time-consuming, and it may minimize the process's overall performance. In addition, scaling up the batch system may not retain the same efficiency. Therefore, the regeneration process of the adsorbent will be complex for large-scale water purification requirements.

A continuous flow system has been investigated in this work, considering the practical application of this method at the industrial level for large-scale water treatment. Adsorbent material was prepared to be suitable for column use and application, regarding granule size and the ratio between supporting material (sand) and the clay (montmorillonite), so it can pass the influent through the column channels. The column system, as a high-efficiency, handle, simple operation, and economical method, has been studied with different parameters that play crucial roles in optimizing the adsorption process for practical applications, including the initial concentration of PHY solution, flow rate, height of the column, and temperature.

Table 3.6

Effect of various parameters on the adsorption removal of PHY in column system

Factors	X	Amount adsorbed	%Removal
Initial concentration (ppm)	20	1.91	96%
	30	2.78	93%
	40	3.44	86%
	50	4.08	81%
Flow rate (ml/min)	2	4.85	97%
	4	4.74	95%
	6	4.29	85%
	8	4.10	82%
	10	3.97	80%
Height of column (cm)	8	4.74	95%
	4	4.32	86%
Temperature of solution (◦C)	10	4.50	90%
	20	4.65	93%
	30	4.75	95%
	40	4.80	96%
	50	4.85	97%

3.3.2.1 Effect of Initial Concentration

To figure out the effect of the initial concentration of adsorbate on the adsorption removal percent of PHY by packing Mnt/sand granules in the column, other parameters were kept constant at flow rate= 10 ml/min, mass= 3g, volume=100 ml, and height= 8cm, at room temperature, with varying adsorbate concentration, ranging from 20 to 50 mg/L.

As Table 3.6 shows, the adsorbed quantity of PHY became larger with increasing the initial concentration of it, thus more molecules flowed through the column, and more adsorption sites were occupied. Therefore, as the initial concentration increased, the percentage of the removal decreased, such that the available adsorption sites would be filled, and the high concentration effluent would raise the amount of non-adsorbed molecules in the effluent.

3.3.2.2 Effect of Flow Rate

Investigations of the impact of flow rate have been performed at 2, 4, 6, 8, and 10 ml/min, as indicated by Table 3.6. Adsorption quantities and capacities were observed to decrease with increasing of flow rate, with an initial concentration of 50 mg/L and constant adjustments to the other parameters. High flow rates caused the adsorbate's residence time in the column to decrease, which resulted in the adsorbate leaving the column before it reached equilibrium due to insufficient residence time, Conversely, using a slow flow rate offering enough time to reach equilibrium between the effluent and adsorbent granules, ended with high adsorbed amount and high percent of removal.

3.3.2.3 Effect of Temperature of Solution

Investigating the temperature of adsorbate solution effect was done with a concentration of PHY 50 ppm, flow rate 10 ml/min, mass 6 g, a height of 8 cm, and volume 100 ml. Temperature control has been achieved by using a circulating water bath in which the solution was immersed, and the temperature ranged between 10 and 50 ◦C.

As the Results revealed in Table.3.6, the percentage of removal increases with increasing temperature, indicating an endothermic adsorption, representing an agreement with the batch system result that has been discussed in section 3.3.1.3

3.3.2.4 Effect of Height of Column

Here is a comparison of the performance of two columns with different inner diameters (10, 7 mm), offering two different heights (4, 8 cm) respectively, and they were backed with the same amount of Mnt/sand (3 g), under particular conditions maintained uniformly. The adsorption efficiency and amount adsorbed of PHY increased with smaller diameter and longer bed depth, according to the results shown in Table 3.6.

Those results can be explained by saying that a longer column provides longer channels for the fluid containing PHY to travel through, which means a longer contact time between adsorbent particles and the PHY fluid, offering better adsorption performance. The adsorption capacity can relate to the larger surface area of taller columns, in other words, larger active sites for adsorption to occur.

3.3.2.5 Column Reusing

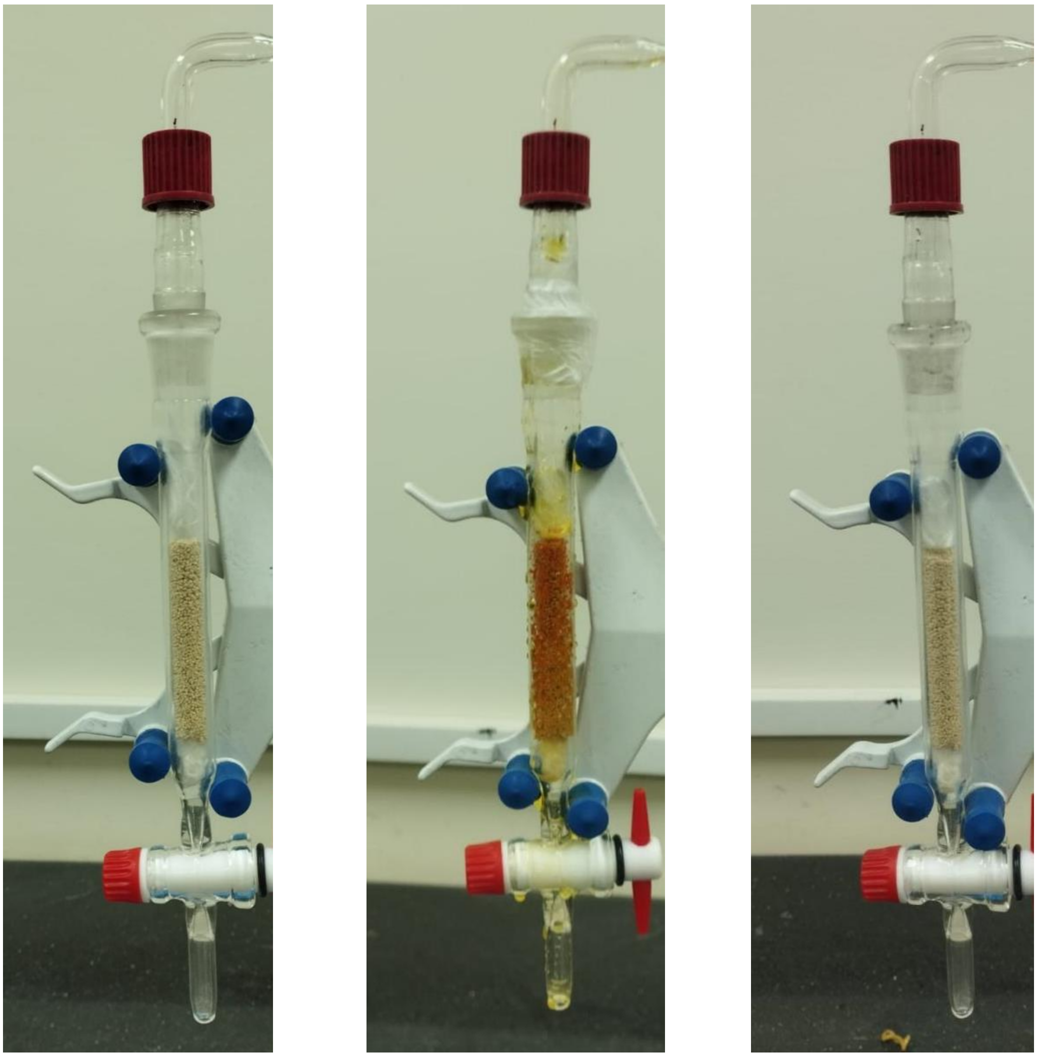
One of the most crucial advantages of the column system is the easy regeneration and reuse processes, which are carried out without the need for additional techniques like centrifuging and sampling. According to TGA results, the column is heated to 550 °C for

2 h, which is the temperature of thermolysis associated with the adsorbate (for pure PHY hydrochloride). The reusing experiment was conducted at room temperature using 6 g of Mnt/sand backed in the column that was 8 cm high, pumping 200 ml of 50 ppm PHY concentration at the flow rate of 10 ml/min.

The results of the seven reusing experiments shحow a non-significant change in adsorption efficiency. With roughly the same percentage of adsorbate removal in each reuse, as revealed in Table 3.7.

Figure 3.6

A picture of the Mnt/sand filtration column at different stages during the adsorption-thermal regeneration process, presenting the fresh Mnt/sand before adsorption, after adsorption, and after thermal regeneration



(a)
Before adsorption

(b)
After adsorption

(c)
After thermal regeneration

The ability of Mnt/sand columns to regenerate and reuse as an adsorption technique for PHY removal is a crucial feature from a sustainability and economic point of view. This feature not only offers a cost-effective and long-term viable method, but it also reduces the need for continuing replacement of the backed adsorbent. Reused Mnt/sand's high adsorption efficiency shows that it is stable and permanent, maintaining its adsorption capacity even after several cycles of use. PHY is just a model of the most prevalent pollutants, which are pharmaceutical compounds. So, the reuse of Mnt/sand on other applications for pharmaceutical contaminated water can present additional benefits and spotlight on valuable performance, flexibility, and limitation for a variety of pollutants, which donate additional research and practical applications.

Table 3.7

The efficiency of the Mnt/sand filtration column for PHY removing the first six cycles of adsorption experiments

% Removal	90%	89%	88%	89%	87%	89%
Reusing experiment no.	1st	2nd	3rd	4th	5th	6th

Note: Initial concentration (50 ppm), Mnt/sand amount (6.0 g), flow rate (10 ml/min). temperature of thermal regeneration (550 ◦C).

3.3.2.6 Effect of Thermolysis Temperature

The thermolysis temperature of an adsorbate is the specific temperature at which the molecule of adsorbate breaks down by heating it into two or more stable and simple molecules, such as water and carbon dioxide, that are released from the thermolysis of organic compounds [105].

Thermogravimetric analysis (TGA) is used to determine the thermolysis temperature of pure PHY hydrochloride, which is obtained to be equal to 650 C, dependent on this result, thermal regeneration of the PHY-contaminated Mnt/sand was suggested to be applied at this temperature. Nevertheless, other experiments done with lower temperatures, as confirmed in Table 3.8, ranging from 650 to 350 ◦C, showed the same efficiency of removal for PHY, then started to decrease by a nonsignificant percentage. Showcase evidence of adopting a lower temperature in the thermolysis process.

This outcome adds greater advantages in terms of energy consumption, cost, and environmental impact, with lower temperatures resulting in lower energy consumption.

To further investigate and explain these findings a computational study was applied on PHY and the surface layer of Mnt/sand adsorbent (Montmorillonite).

Table 3.8

Effect of Thermolysis Temperature on the Adsorption Performance

Temp of thermolysis	350	450	500	550	600	650
% Removal	97.37%	98.12%	98.19%	98.24%	98.25%	98.24%

3.3.2.6 Computational Study of PHY Adsorption on Montmorillonite

The thermolysis technique used in the regeneration of Mnt/sand was done at 650 ◦C (PHY decomposition temperature in a free state which was determined by the TGA result), which offers sufficient energy to completely decompose of PHY in its free state, nevertheless, when the adsorbate molecule adsorbed, it doesn't just stick to the adsorbent surface, otherwise the molecules internal bonds can be affected, both in length and strength and this can be related to multiple factors such as electronic interaction, catalytic effects, hydrogen bonding formation, Van Der Waals forces.

A computational investigation was applied in this study to observe the consequences of PHY adsorption onto the Mnt surface, giving insight into adsorbate-adsorbent interaction as a simulation study, concerning the bond lengths of the phenazopyridine molecule before and after adsorption. The study was done and supported using the Density Functional Theory (DFT), a powerful computational modeling method for simulation and prediction of the adsorption mechanism, which can detect structure changes and obtain the interaction and forces involved through the adsorption process. The bond length indicates this bond's strength and thus can be related to the energy required to break it down, particularly through the decomposition process in thermal regeneration.

As the results shown in Figure 3.7 (1), one of the main factors that affect the adsorption process is the hydrogen bonds, such as the ones observed between the hydrogens of the two amino groups ($-NH_2$) attached to the pyridine ring of the PHY molecule and the oxygen atoms related to Mnt cell (Si-O), referred to (a) in the structure (1), in addition, hydrogen bond formed between the protonated azo group and the Mnt oxygen referred to (b) in the structure (1).

By performing DFT calculations, the bond lengths of both free molecule and adsorbed molecule could be obtained for each case, as Figure 3.7 (4) and (5) shows, there is length change of the bond before and after adsorption, and for comparing these calculated bond lengths the different was measured in Table B.1, where it could be considered as a significant change when its greater than 0.010 A◦ [106]. Table B.1 presents the amount of elongation for several bonds ranging between 0.013- 0.021 A◦.

In general, adsorption involves the formation of new interactions between the adsorbate and the adsorbent surface, consequently, disorganizing the electron distribution in the adsorbate molecule. In return for the formation of these hydrogen bonds (and other secondary bonds) between the phenazopyridine molecule and the Mnt surface, there is lengthening and weakening of some bonds in the phenazopyridine molecule which means they are easier to break, so the thermolysis process is directed towards these weaker bonds with lower energy needs to break it, and it continued to a series of reactions until it completely convert to the simplest substance. This explains the reduction in energy consumed in the thermolysis of adsorbed phenazopyridine on the Mnt surface. These results support applying thermolysis regeneration technique at a lower temperature than 650 °C, which achieves the desired goal by saving maximum energy that can be saved.

Moreover, the geometry of phenazopyridine that is correlated to the structure stability also plays a role in the thermal energy reduction for thermolysis of adsorbed molecules, as Figure 3.7 (2) shows the geometry of free state phenazopyridine, on the other hand, when it was adsorbed on the surface of adsorbent, the structure has been distorted as it confirmed in Figure 3.7 (3), give an additional reason for easier bond breaking of the molecule, thus reducing the energy consumption required for decomposition. Furthermore, to make sure that the PHY was fully fragmented down by its thermal degradation at lower temperatures, regenerated adsorbent samples were analyzed by FT-IR, which were decomposed at temperatures lower than 650°C. as the result showed in Figure A.8, the temperature of 550°C was found to completely eliminate the PHY peaks while preserving absorption efficiency.

the column, Figure A.1 shows the concentration of the effluent that leaves the Mnt/sand filtration column over time.

At the beginning of the continuous adsorption run the effluent starts to exit completely purified (percent of removal 99.8%), such that the first arriving PHY molecules will be in direct contact with abundant empty active sites on the surface of naked Mnt/sand granules, which will capture the majority of them and the liquid drops almost pure. Gradually, the concentration of the contaminant started to increase in the effluent, with less efficient sites on the surface of the adsorbent.

The percentage of removal throughout the first 51 minutes ranged between 99-84%. The point when the concentration of adsorbate in the effluent reaches about 5 ppm after 48 minutes, implies that the breakthrough time has passed, which is defined as the time passed from the first moment of starting the continuous adsorption process until the concentration of the adsorbate-contaminated effluent reached an agreed level (about 10% from the initial concentration). After the breakthrough point, the concentration of PHY in the effluent increases rapidly till it approaches the exhaustion point, which indicates a high saturated level in the adsorbent, prevents any additional adsorption occurring after this point, making the concentration of the effluent constant in close proximity to the initial concentration, even with further time of flowing.

Chapter Four

Conclusion and Recommendation

4.1 Conclusion

This study exposed a new sustainable and practical technique for water purification from phenazopyridine hydrochloride (PHY) as a pharmaceutical pollutant model. The technique depends on adsorption followed by a thermolysis process, ensuring the effective removal and then the thermal decomposition of PHY. This novel recovery technique allows for multiple reusing cycles, maintaining the efficiency of performance, which was applied for both the column system and batch system. The utilization of montmorillonite/sand composite (Mnt/sand) as an adsorbent showed respectable removal efficiency, with the adsorption capacity of 8.89 (mg/g). Therefore, the optimum percentage of PHY removal in the batch system was 95% when Mnt/sand dosage was 0.5 g, for PHY concentration of 20 ppm, under adjusted conditions (pH 5, 25 ◦C).

A set of parameters was investigated for the batch system to determine the optimized conditions, where PHY adsorption increased at the acidic medium, reaching its optimal value at 5 (which is around the natural pH for PHY solution), and it decreased in the basic medium pH (8-10). The percentage removal of PHY increased as the amount of Mnt/sand increased. The inverse relation with the concentration of PHY, such as the adsorbing removal percent decreased with increasing the initial concentration. The results detected the adsorption during a contact time of 60 minutes, but most adsorption is acquired within the first 20 minutes, at which point equilibrium is reached.

The Langmuir isotherm model described the adsorption behavior, suggesting monolayer adsorption with a homogeneous adsorbent surface, and the kinetics results showed that PHY adsorption on Mnt/sand can be represented by pseudo-second order, and calculating the activation energy indicated that the adsorption process can follow a combination mechanism between chemical and physical mechanisms. Thermodynamic parameters values indicated spontaneous and endothermic adsorption, pointing to a strong affinity between PHY and Mnt/sand.

Continuous adsorption experiments were investigated in the column system with various parameters involving flow rate, concentration, effluent temperature, and column height.

Under optimized column parameters (10 ml/min, 50 ppm, 6 g, 25 °C, pH 5), the results showed an excellent percent of removal equal to 97%. This study supports and proves the ability of Mnt/sand to be used in a large-scale water purification application as a continuous flow procedure.

Thermolysis decomposition, a nontraditional technique for recovering the polluted adsorbent, was used to eliminate PHY adsorbed on the Mnt/sand surface by turning PHY into CO_2, H_2O, and other gases at 650 ◦C. Computational study and thermolysis temperature study were applied to investigate the ability to lower temperature needs in thermolysis, resulting with 550◦C as an effective value for this process, maintaining the adsorption efficiency for many cycles (up to 6 for the column). Adsorption-thermolysis cycles explored in this work proposed a revelation technique in the world of water purification as a reliable, economical, simple, and reusable technique for water treatment from pharmaceutical pollutants.

4.2 Recommendations

This research paves the road for additional adsorption experiments on different pharmaceuticals, dyes, and other organic pollutants using this prepared adsorbent (Mnt/sand). In addition to single solution effluent, a binary solution effluent of two different contaminants and a real wastewater solution are recommended in future works. Other clays such as bentonite, zeolite, and kaolinite can be used instead of montmorillonite, studying their adsorption efficiency for both the batch system and column system.

Theoretical study for the column system needs more investigations using different dynamic adsorption models, such as Bed Depth Service Time (BDST) model and Thomas model, that analyze the breakthrough curves of the adsorption columns and determine the optimized column parameter for a real-life application.

Furthermore, computational studies open the door to various analyses, including adsorption energy calculation and molecular dynamic simulation of adsorbate-adsorbent interaction, which present the possible scenarios before our eyes or even support the actual experimental results and prove them.

List of Abbreviations

Symbol	Abbreviation
PHY	Phenazopyridine hydrochloride
Mnt/sand	Montmorillonite/Sand Composite
Ea	Activation energy
K	Adsorption equilibrium constant
q_e	Amount of adsorbate per unit of adsorbent
A	Arrhenius constant
C_t	Concentration of adsorbate in the solution at time t
C_o	Initial concentration of adsorbate in the solution
C_e	Equilibrium concentration of adsorbate in the solution
R^2	Correlation Coefficient
K_f	Freundlich isotherm constant
R	Ideal gas constant
b	Langmuir isotherm constant
m	Mass of adsorbent
V	Volume of aqueous solution
Q_o	Maximum monolayer coverage capacity constant at equilibrium
PZC	Point of zero charge
FT-IR	Fourier transform infrared spectroscopy
SEM	Scanning electron microscopy
TGA	Thermogravimetric Analysis
XRD	X-ray diffraction

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Appendices

Appendix A

Figures

Figure A.1

Breakthrough curve of PHY removal by Mnt/sand filtration column

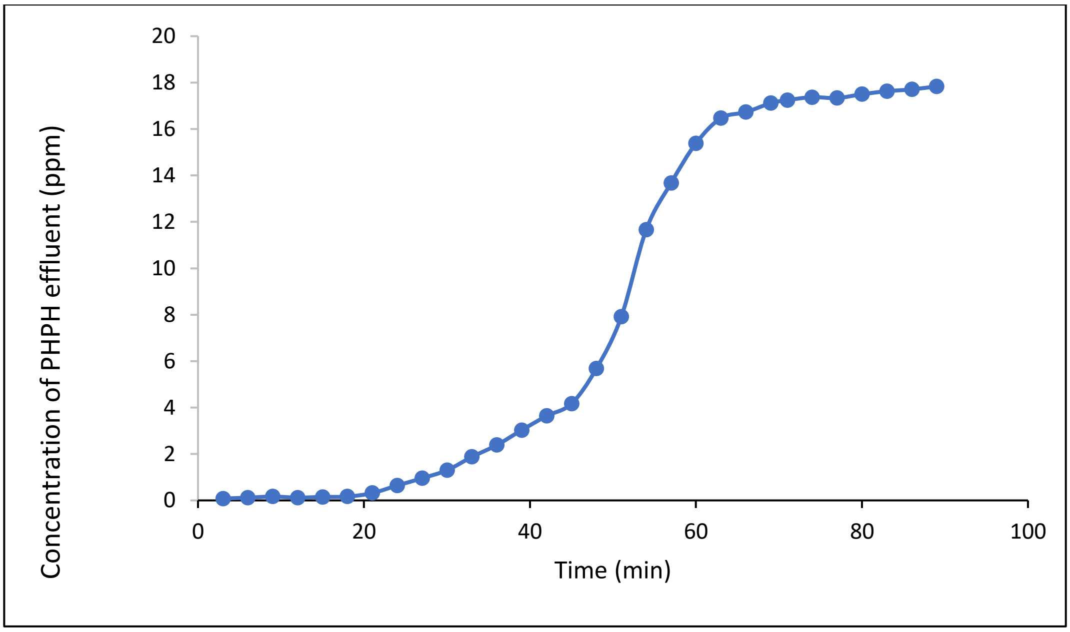


Figure A.2

The efficiency of the Mnt/sand filtration column for PHY removing the first six cycles of adsorption experiments. Initial concentration (50 ppm), Mnt/sand amount (6 g), flow rate (10 ml/min). temperature of thermal regeneration (550 ◦C)

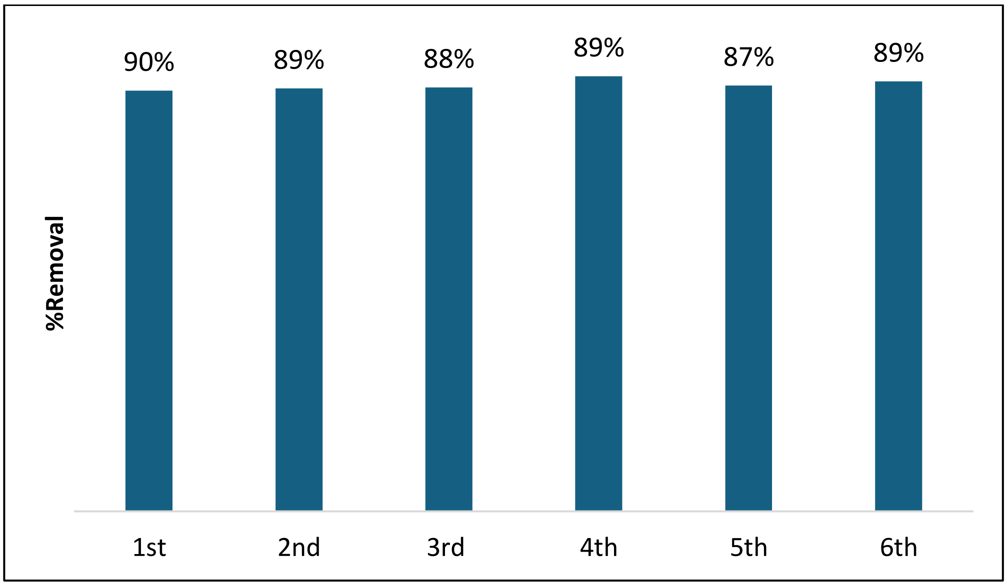


Figure A.3

Effect of initial concentration of PHY influent on adsorption efficiency of removal. At flow rate (10 ml/min), Mnt/sand amount (3 g), at room temperature. temperature of thermal regeneration (550 ◦C)

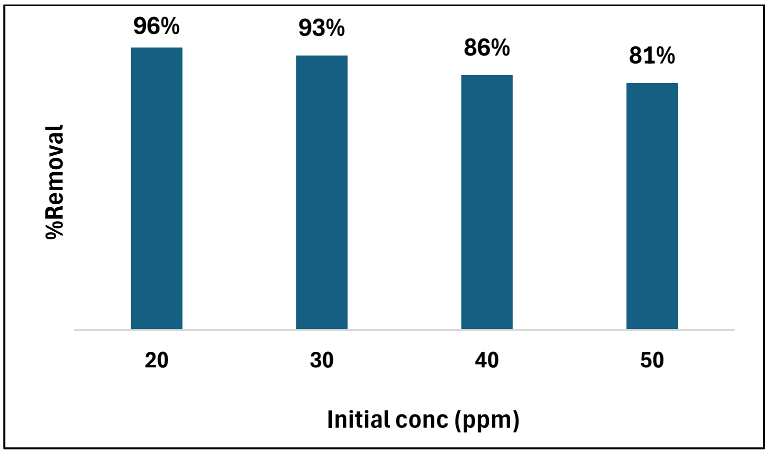


Figure A.4

Effect of flow rate on adsorption efficiency of removal. Initial concentration (50 ppm), Mnt/sand amount (3 g), at room temperature. temperature of thermal regeneration (550 ◦C)

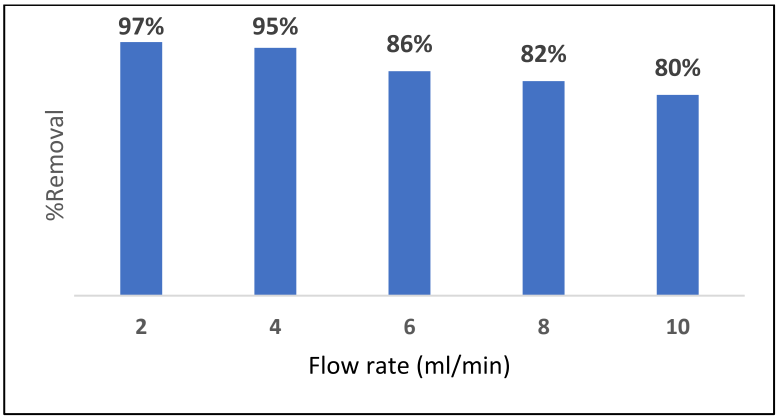


Figure A.5

Effect of temperature on adsorption efficiency of removal. Initial concentration (50 ppm), Mnt/sand amount (6 g), flow rate (10 ml/min). temperature of thermal regeneration (550 ◦C)

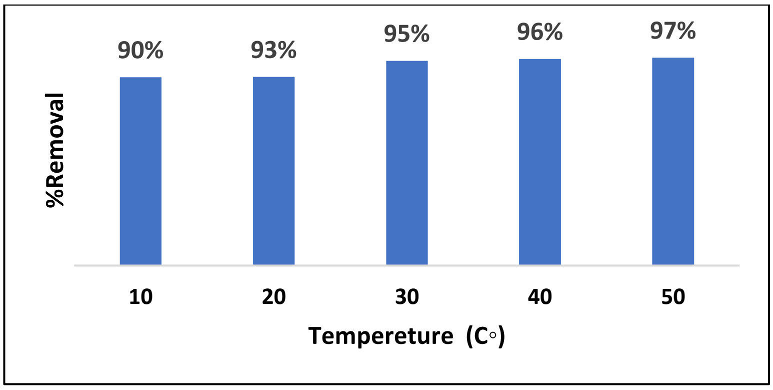


Figure A.6

Effect of column height on adsorption efficiency. Initial concentration (50 ppm), Mnt/sand amount (3 g), flow rate (4 ml/min). temperature of thermal regeneration (550 ◦C)

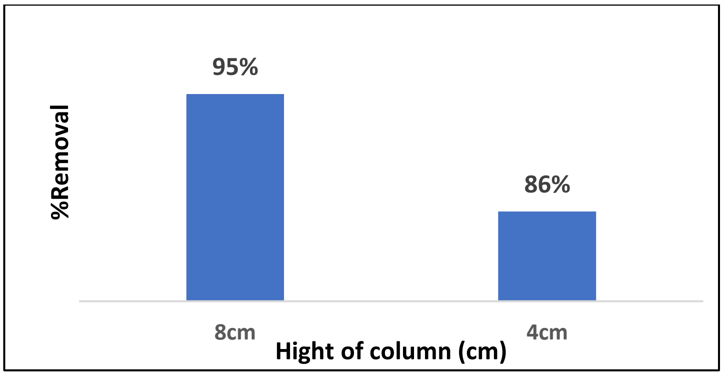
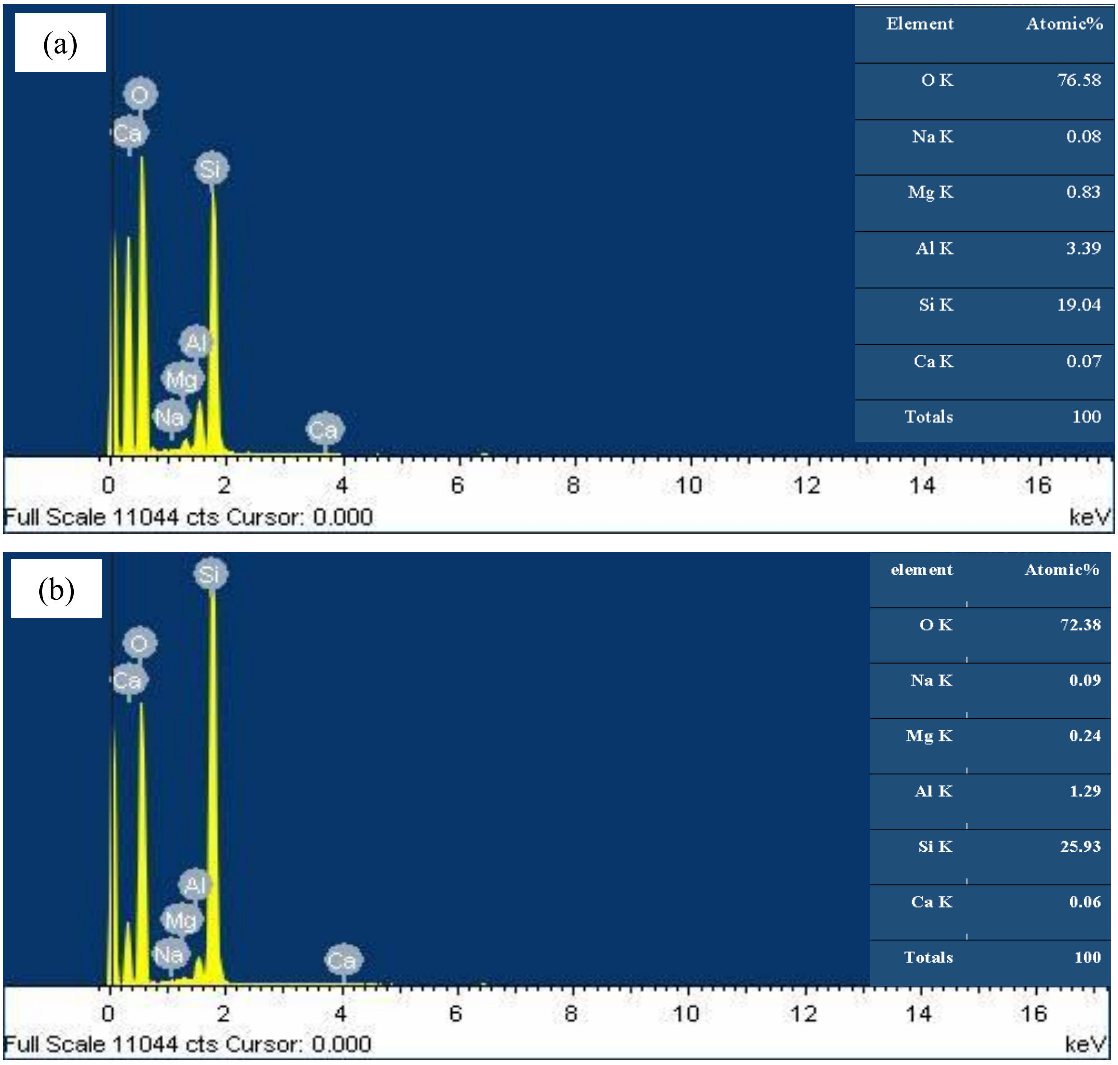


Figure A.7

SEM results



Element	Atomic%
O K	76.58
Na K	0.08
Mg K	0.83
Al K	3.39
Si K	19.04
Ca K	0.07
Totals	100

element	Atomic%
O K	72.38
Na K	0.09
Mg K	0.24
Al K	1.29
Si K	25.93
Ca K	0.06
Totals	100

Note: (a) Composition of montmorillonite. (b) Composition for Mnt/sand**.**

Figure A.8

IR-spectra for regenerated Mnt/sand at 550 C, and fresh Mnt/sand sample.

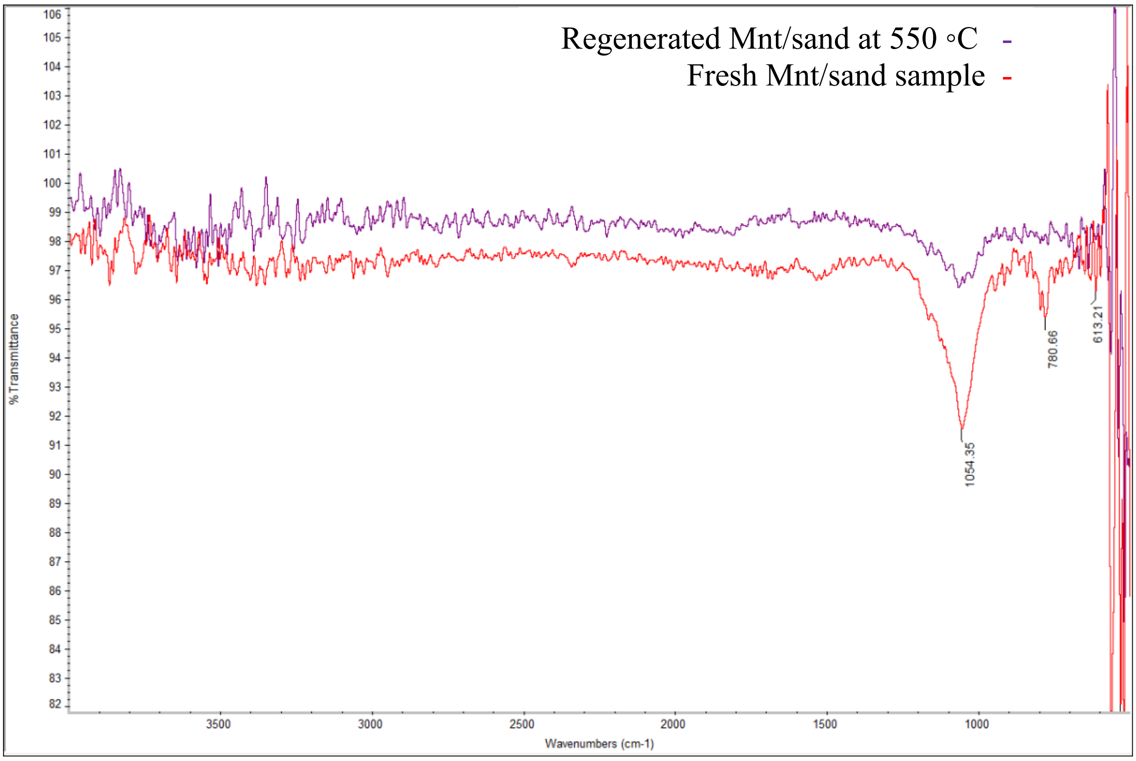


Figure A.9

Percent of PHY removal versus amount of adsorbent (optimization the amount of adsorbent used in the batch system). PHY solution of initial concentration 20 ppm, 100ml, pH 5, at room temperature

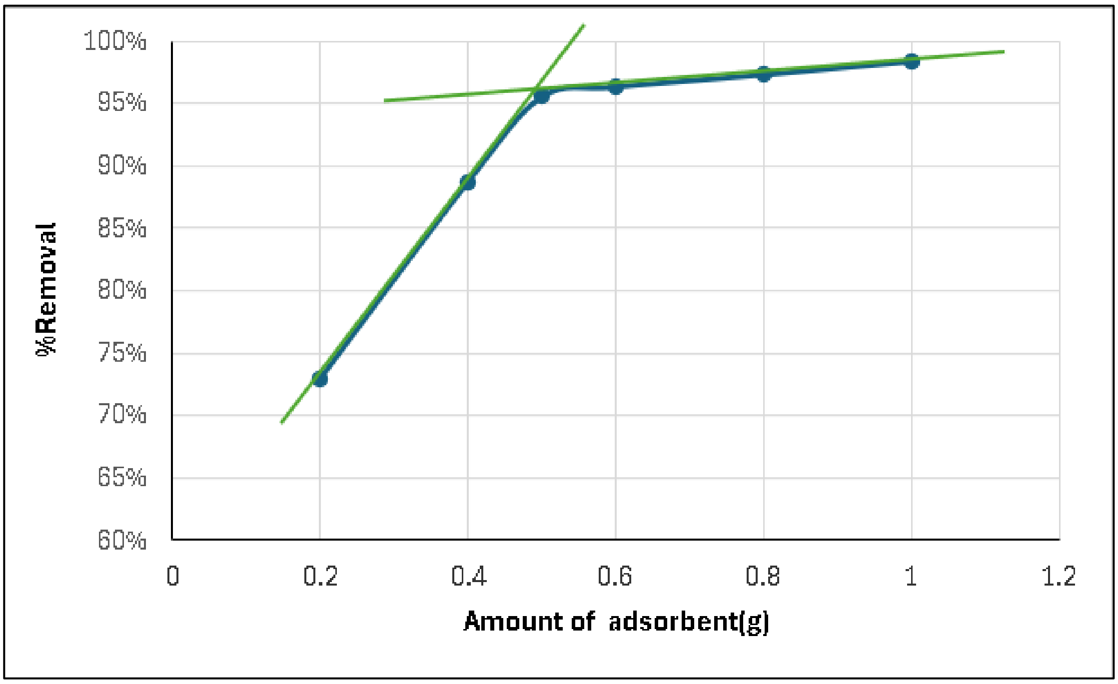
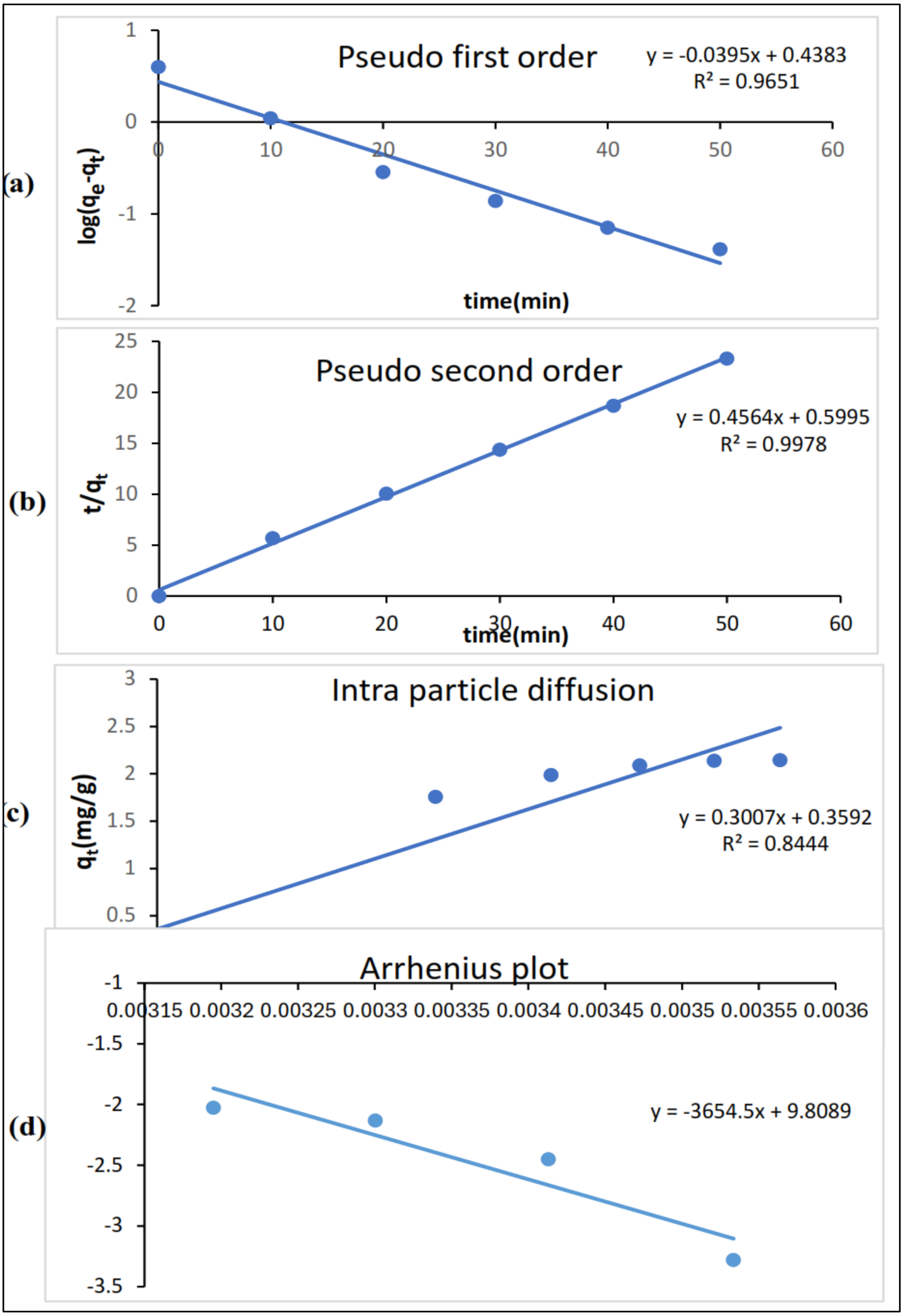


Figure A.10

Kinetics of phenazopyridine removal



Note: (a) the pseudo-first-order model, (b) the pseudo-second-order model, and (c) the intra-particle diffusion model, (d) Arrhenius plot (lnK versus 1/T)

Figure A.11

Effect of Mnt/sand amount on(a) removal and(b) adsorption capacity of PHY

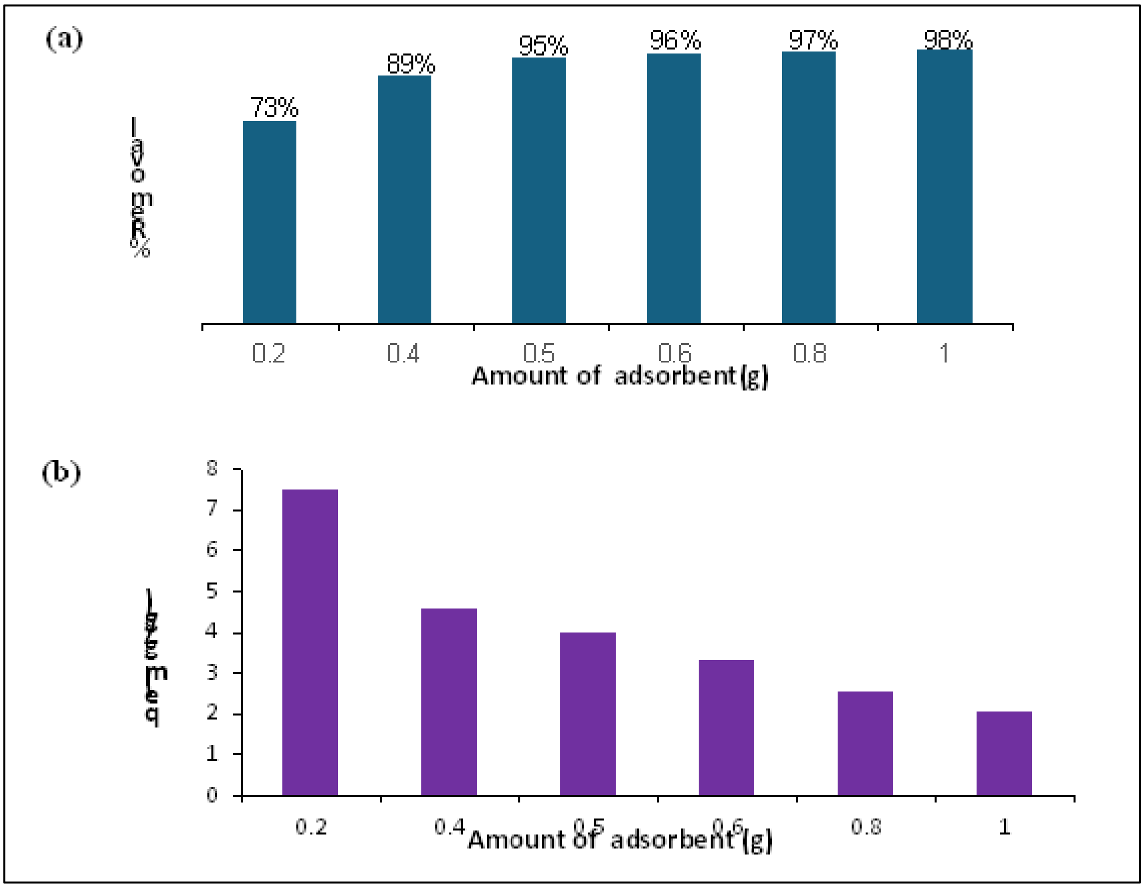


Figure A.12

The efficiency of the Mnt/sand adsorbent for PHY removal in the first five cycles of adsorption experiments

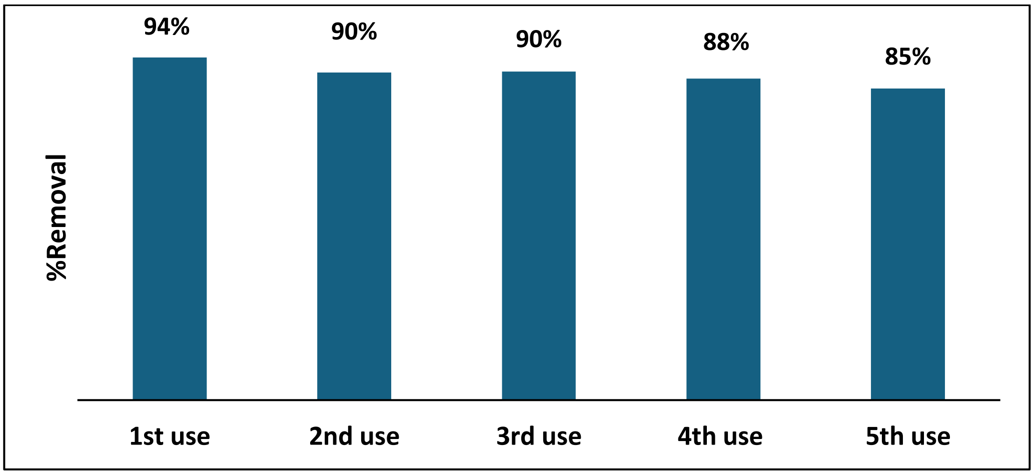
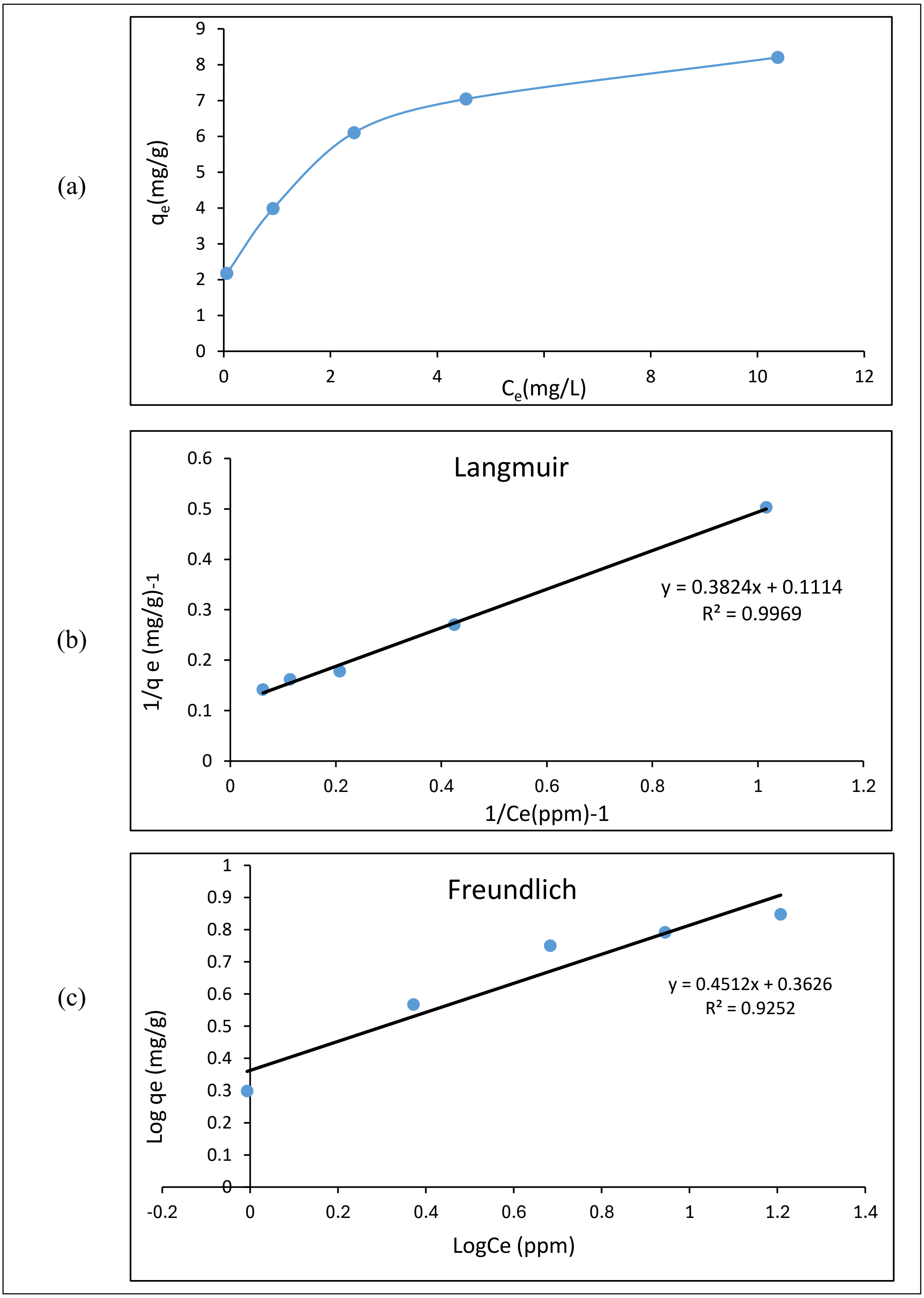


Figure A.13

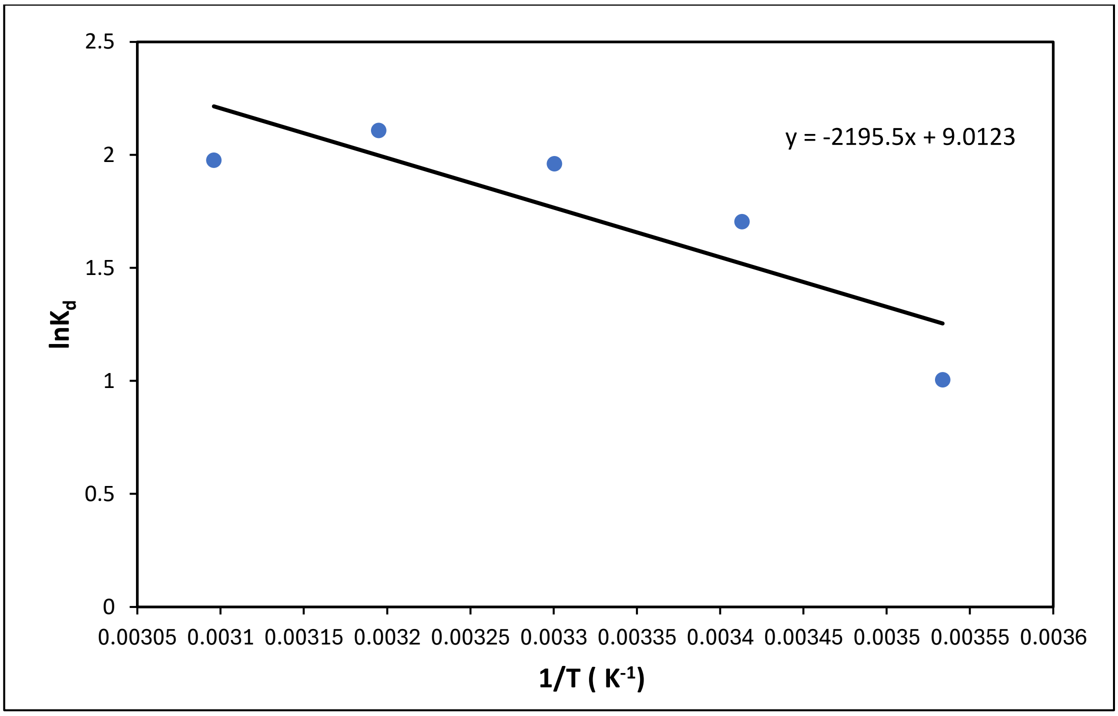
Equilibrium adsorption isotherms (temperature: 25◦C, initial pH: 5 and solid/liquid ratio 0.5 g/100 mL)



Note: (a) Equilibrium adsorption isotherm of PHY onto Mnt/sand. (b) Langmuir isotherm for adsorption of PHY onto Mnt/sand. (c) Freundlich isotherm for adsorption of PHY onto Mnt/sand.

Figure A.14

Plot of Ln K_d versus 1/T for ΔH° and ΔS° determination. (30 ppm PHY, 100 ml of solution, 0.5g of Mnt/sand, pH 5)



Appendix B

Tables

Table B.1

Bond lengths of some bonds of phenazopyridine molecule before and after adsorption by DFT simulation using GFNn-xTB method

Bond symbol	Bond length before adsorption (A◦)	Bond length after adsorption (A◦)	Degree of elongation (A◦)
C1-C2	1.382	1.395	0.013
C1-C3	1.382	1.395	0.013
C8-C10	1.342	1.355	0.013
C9-C11	1.439	1.453	0.014
N3-C9	1.303	1.319	0.016
N1-N2	1.257	1.276	0.019
N5-C7	1.316	1.337	0.021

جامعة النجاح الوطنية
كلية الدراسات العليا

تحضير واستخدام مركب من المونتموريلونيت/الرمل المستقر حراريًا لإزالة الفينازوبيريدين من الماء بالامتزاز، متبوعًا بالتجديد الحراري: قابلية إعادة الاستخدام في أنظمة الدُفعات والتدفق المستمر

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عاهد حسني عبد الرزاق زيود

قدمت هذه الرسالة استكمالا لمتطلبات الحصول علي درجه الماجستير في الكيمياء، من كلية الدراسات العليا، في جامعة النجاح الوطنية، نابلس– فلسطين.

2025

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الملخص

تُعد حماية الماء ضرورة حيوية كونه أساس الحياة، إلا أن التلوث الدوائي للمصادر المائية أصبح تحديًا عالميًا، نتيجة التطور الصناعي والصيدلاني وما يصاحبه من تصريف نفايات صناعية وبشرية إلى المياه. ولهذا، تتجه الأبحاث لإيجاد طرق فعالة، منخفضة التكلفة، وصديقة للبيئة لتنقية المياه.

تركز هذه الدراسة على إزالة مادة دوائية ملوثة، وهي فينازوبيريدين هيدروكلوريد (PHY) باستخدام ممتز مركب من المونتموريلونيت والرمل، (Mnt/sand) يتم تجديده عن طريق التحلل الحراري. نُفذت التجارب في نظامي الدفعة والعمود، مع اختبار تأثير عدة متغيرات مثل: الرقم الهيدروجيني، التركيز الابتدائي، كمية الممتز، ودرجة الحرارة.

في نظام الدفعة، كانت الكفاءة الأعلى عند pH 5 بنسبة إزالة 96% من محلول بتركيز 20 جزء في المليون في غضون 20 دقيقة عند 25 درجة مئوية. وُجد أن كفاءة الامتزاز تقل عند زيادة تركيز PHY أو في الوسط القلوي. أما نموذج لانجمير فقد وصف الامتزاز بدقة ($R^2 = 0.99$)، مشيرًا إلى امتزاز أحادي الطبقة على سطح متجانس. واتبعت العملية نموذج الترتيب الظاهر الثاني، مع طاقة تنشيط بلغت 30.4 كيلوجول/مول، وديناميكا حرارية تشير إلى أن الامتزاز تلقائي وماص للحرارة. أما في نظام الأعمدة، فلوحظ أن تقليل معدل التدفق والتركيز الابتدائي، وزيادة ارتفاع العمود، يعزز الكفاءة. تم تحديد الظروف المثلى

عند: 10 مل/د، تركيز 50 جزء في المليون، 6 غم ممتز، ارتفاع عمود 8 سم، pH 5، ودرجة حرارة 25°س، محققة كفاءة 97%.

أكدت تقنيات التحليل (XRD, SEM, TGA, FT-IR) بنية الممتز وخصائصه، بما في ذلك الاستقرار الحراري للممتز. ومن خلال التحلل الحراري عند 650°س، تم إزالة PHY نهائيًا دون فقد كفاءة الممتز، مع إثبات إمكانية تخفيض درجة الحرارة إلى 550°س دون تأثير سلبي.

ختامًا، تُظهر الدراسة أن تقنية الامتزاز–التحلل الحراري باستخدام Mnt/sand تمثل حلاً فعالًا، اقتصاديًا، وقابلاً لإعادة الاستخدام لتنقية المياه من الملوث الدوائي PHY .

الكلمات المفتاحية: الامتزاز؛ الممتز؛ المونتموريلونيت؛ الرمل؛ هيدروكلوريد فينازوبيريدين؛ نظام العمود؛ نظام الدفعات؛ التحلل الحراري.