SYNTHESIS AND CHARACTERIZATION OF IRISH POTATO PEELS POWDER-NANOSILICA COMPOSITE FOR THE DEGRADATION OF RHODAMINE BLUE AND DICLOFENAC

JOSEPH NZUKU MUTIE

A Thesis Submitted to the Graduate School in Partial Fulfillment of the Requirement for the Award of Master of Science Degree in Chemistry of Chuka University

CHUKA UNIVERSITY
SEPTEMBER, 2023

DECLARATION AND RECOMMENDATION

Declaration

This thesis is my original work and it has not been submitted for award of diploma or conferment of a degree in any other university.

Signature: ……………………………… Date 18/09/2023 ………………
Mutie Joseph Nzuku
SM11/29280/17

Recommendation

This thesis has been examined, passed and submitted with our approval as the University Supervisors.

Signature……………………………… Date 18/09/2023 ………………
Prof. Joel Mwangi Gichumbi, PhD
Chuka University

Signature……………………………… Date 18/09/2023 ………………
Prof. Ochieng Ombaka, PhD
Chuka University

18 SEP 2023

ACKNOWLEDGEMENT

To begin, I'd want to express my deepest thanks to my supervisors, Prof. Joel Mwangi Gichumbi and Prof. Charles Ochieng Ombaka, for giving me unwavering support, constructive criticism, encouragement, advice, and motivation during my studies. In addition, I'd like to thank Juliet Makau, Eric Lihanda, and Chrispine Odhiambo for their help with UV-VIS and FTIR analysis.

My thanks also go to the employees of the department of Geology and Mines Nairobi, Kenya for their assistance during data analysis, without forgetting the support received from my course mates in terms of ideas and advice. Further, I 'd want to thank Chuka University for allowing me to study for this course. Furthermore, the patience, financial, and support encouragement of my family members can’t go unacknowledged and unappreciated. Above all, I thank God for blessing me with excellent health and sufficient of grace during my studies.

DEDICATION

The work is dedicated to my father, Morris Nzuku, my mother, Lydia Morris, my dear wife, Winjoy Joseph, and my beloved son, Shawn Baraka for the continued support through my academic journey. Further dedication to my late grandmother Elizabeth Mwikali, for her invaluable contribution through my academic journey.

COPYRIGHT

ABSTRACT

In today's world, finding safe drinking water has become a major concern. Many contaminants, including dyes and pharmaceuticals, are discharged directly or indirectly into bodies of water without sufficient treatment, rendering the water unsafe for human consumption. To safeguard the environment and human health, harmful toxins must be removed from wastewater. Various technologies have been used to address this issue. Adsorption on activated carbons is a widespread technique in wastewater treatment, but the exorbitant cost of ordinary activated carbons limits its use. Several agricultural waste products are currently being used inefficiently and have the potential to be transformed into important adsorbents such as composites. Because of its nano-sized inorganic filler, nano-silica has exceptional characteristics such as large surface area, mesoporous structure, biocompatibility, versatile pore size, modifiability, and polymer hybridizability over common composites. Irish potato peel powder is a natural binder that works well in composite materials. Since most composite materials are poorly distributed, this study concentrated on utilizing Irish potato peel powder and nano-silica from rice husks to produce a composite of Irish potato peel powder and nano-silica. This study aimed to synthesize, characterize and make Irish potato peel powder/nano-silica composite in the degradation of rhodamine blue and diclofenac. Silica nanoparticles were mixed with Irish potato peel powder in the ratios 1:1, 1:2, 2:1, 4:1, and 5:1, respectively. Glutaraldehyde was added to the mixture as a binder. The following functional groups was detected in the composite's Fourier Infrared spectrum: C=C, O-Si-O, and Si-OH, which corresponded to peaks at 1645.35 cm^{-1}, 1104.29 cm^{-1}, and 3439.23 cm^{-1}, respectively, and are responsible for the adsorption of Rhodamine Blue and Diclofenac. The XRF analysis showed that silica accounted for a large proportion in the composite, which determined the mixing ratio of RHNS and IPPP (4:1). The composite surface area was 100.6328 m^2/g, with a single point surface area of 97.4036 m^2/g, according to BET-BJH surface characterization. The synthesized composite was amorphous in nature, as shown by the XRD pattern, which has a strong broad peak between 20^0 and 25^0 (2θ). The adsorption capacity of RB and DCF by the composite was optimal at pH 4 and 2, respectively, an initial concentration of 1 mg/L and 40 mg/L, respectively, an adsorbent dose of 0.1 g, and a 240 rpm stirring speed. The removal efficiency of the composite was 99.39% for DCF and 97.57% for RB. The rhodamine blue removal best fit the Freundlich isotherm in the used composite adsorbent with $R^2 = 0.996$, while the DCF removal suited the Langmuir isotherm model the best with $R^2 = 0.901$. The kinetic data were pseudo-second-order ($R^2 = 0.9989$ for RB and 0.849 for DCF), which was more suitable for explaining the adsorption rate. Fineness, surface area, and vacancy concentration are all associated with better adsorption capacity.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ACRONYMS AND ABBREVIATIONS

BET	Brunauer–Emmett–Teller
BJH	Barrett-Joyner-Halenda
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
DCF	Diclofenac
EU	European Union
FTIR	Fourier Transform Infrared Spectroscopy
IPPP	Irish Potato Peels Powder
IPPP-NSC	Irish Potato Peals Powder-Nano Silica Composite
IPPs	Irish Potatoes Peels
ISO	International Organization for Standardization
NEMA	National Environment Management Authority
NSAID	Nonsteroidal Anti-Inflammatory Drug
Ops	Organophosphorus Pesticides
PACs	Pharmaceutically Active Compounds
pH	Power of Hydrogen
PCPPs	Personal Care Products and Pharmaceuticals
Q_m	Maximum Sorption Capacity, (mg/g)
RB	Rhodamine Blue
RHA	Rice Husk Ash
RHNS	Rice Husk Nanosilica
UK	United Kingdom
UNDP	United Nations Development Programme
UNEP	United Nations Environment Programme
USA	United States of America
WHO	World Health Organization

CHAPTER ONE

INTRODUCTION

1.1 Background of Study

Water quality has worsened due to the development of new technologies and population expansion. Environmental disturbances and a growing pollution problem are the results of the rapid rise of new technology and population growth. It has been demonstrated that anthropogenic activities significantly affect the quality of water. Water contamination is a global problem, so scientists are devising new methods to combat it (Schwarzenbach *et al*., 2010). Removing pollutants from water is an urgent necessity, and devising a method that is both economical and safe for the environment is a challenging task.

Pollution of waters has become a significant hazard to the natural world's water supplies in third-world countries. This occurrence is related to the growing demand for countries to attain industrialization and national development objectives, with Kenya being one of them (Kithia, 2011). Due to the large volume of wastewater generated by factories that contain harmful pollutants such as heavy metals and pigment, industrialization has caused significant damage. The majority of dyes that are not used generate unwanted effluents that are frequently dumped into the natural environment short of sufficient treatment (Dasgupta *et al*., 2015). The spilled industrial water comprises a variety of poisonous and organic elements that are damaging to aquatic organisms (Robinson *et al*., 2001).

Paper, textile, plastics, rubber, pharmaceutical, cosmetic, and food industries all employ dyes (Chequer *et al*., 2011). One of the most polluting industries on the globe is the textile industry. Dyes have an impact on aquatic ecosystems by restricting light penetration in rivers for photosynthesis in addition to detracting from aesthetic value (Modi *et al*., 2010) and Saratale *et al*., 2011). The preponderance of these colors is linked to colon cancer, skin irritation, allergies and dermatitis (Golka *et al.,* 2004). Besides, some dyes are known to be either carcinogenic, toxic or mutagenic (Benson *et al*., 1980). These pigments persist in the environment if not properly treated, presenting a major danger to aquatic existence (Da Silva *et al*., 2011 and Carneiro *et al*., 2010).

According to WHO, coloring substances in drinking should not be more than 1 μgl^{-1}. compliance with new textile quality requirements in the form of ISO 14000 series certification is the first major environmental challenge confronting the textile industry in both industrialized and developing countries, including Kenya (Nawrocka and Parker, 2009). The second reason is growing environmental awareness of consumers and their interest in eco-labelled textile products (Houe and Grabot, 2009). These environmental constraints hinder the growth of export business, particularly in developing countries (UNEP, 2008; UNDP 2005, 2007, 2009). To enable the Kenyan textile industry to compete in global markets, particularly the US, UK and EU; The production of eco-labelled products is necessary, therefore novel technologies based on locally available materials need to be developed to remove dyes from textile wastewater (Houe and Grabot, 2009).

Pharmaceutical is compounds that can be utilized to diagnose, treat, or prevent illness, as well as to repair, correct, or modify organic functioning. Because they are constantly discharged into the environment, they are pseudo-persistent. They can affect water quality and endanger the wellness of humans and the surroundings (Ellis, 2006). Drugs have been proven in research studies to induce harmful consequences such as decreased reproduction, mortality, and impaired growth in marine creatures (Kolpin *et al*., 2002). Diclofenac toxicity in vultures and detrimental effects of pharmaceuticals in terrestrial and aquatic habitats have been stated to have estrogenic effects in fish (Shore *et al*., 2014).

The majority of ecotoxicological investigations of environmental pharmaceuticals have been based usually based on acute exposures, although chronic exposure at low dosages of pharmaceutical combinations is the most concerning (Johnson *et al*., 2008). For a variety of factors, the rate of drug manufacture and subsequent environmental release is predicted to rise during the next few decades. First, as living standards grow, so will worldwide access to and use of medications, particularly in developing nations. Second, as individuals live longer lives, the number of elderly persons increases globally, necessitating the usage of several medications. Third, the rising availability of low-cost generics as a result of patent expirations (Kümmerer, 2010).

This study focused on Rhodamine blue (RB) and pharmaceutical residue, diclofenac (DCF), in the environment. Rhodamine blue is a fresh peach synthetic dye that is frequently used in the culinary and textile plants. Drinking water polluted with RB has been shown in studies to cause subcutaneous tissue-borne sarcoma (Jain *et al.*, 2007).

The methods currently used to remediate dyes and drugs in wastewater are chemical oxidation, activated carbon adsorption and microbial methods. However, the mentioned technologies don’t demonstrate effective removal rates or economic benefits (Crini, 2006). Considering activated carbon, which is the most common and frequently used adsorbent for dyes and medicines, however it has several drawbacks. Despite its widespread application in adsorption processes, the main disadvantage of its use in industry is its high cost and difficulty in regeneration. In addition, regeneration with solutions results in a small amount of additional wastewater, while recycling using torrid technology results in a ten to fifteen percentage loss of sorbent and holding capacity (Robinson *et al.*, 2001).

As research in using low-cost, readily available and cheap biomaterials for adsorption of dyes is growing, the feasibility of Irish potato peels and nano-silica composite as adsorbents for the removal of RB and DCF from solutions is being investigated. Natural adsorbents previously studied for dye removal include *Jatropha curcas*, sugarcane bagasse (Kadam *et al.*, 2013), filamentous green alga Spirogyra sp (Khataee *et al.*, 2013), wood sawdust (Mane and Babu, 2013), spent brewer's grain (Chanzu *et al.*, 2012), pine waste treated with acid and raw pine powder (Dawood and Sen, 2012), and sugar beet pulp (Vučurović *et al.*, 2012). These agricultural waste adsorbents have low adsorption capacities, hence there is need to produce adsorbents with better adsorption capacity and therefore use nanocomposites (Khataee *et al.*, 2013).

Rice husk as a waste material is produced in high amount in developing countries. It is utilized as a fuel source for boilers in rice mills, as a construction material and also as a fertilizer in some industries (Pode, 2016). However, the accessible quantity of rice husks surpasses all of these local uses, and disposal issues exist. Rice husk is a potential adsorbent because it has 15-22% SiO_2 in hydrated amorphous state, which is an excellent adsorption, like silica gel (Haris *et al.*, 2011).

Irish Potato peels (IPPs) are produced as waste in industries that potatoes to produce chips, starch and crisps. The estimated world production of IPPs is eighty thousand tonnes per year. The peels are commonly used for production of biogases, feedstock and fertilizer (Anastopoulos and Kyzas, 2014). However, the accumulation of these peels poses a burden to the environment. Recycling these wastes into a cost-effective, multifaceted adsorbent for removing, dyes, heavy metals and drugs would be a method of eliminating these pollutants while also purifying wastewater. Since most composites face the problem of homogenization, there is a need to use binders and hence the use of IPPs rich in high-value components, especially starch and lignin, which are natural binders (Dufresne, 2010).

1.2 Statement of the Problem

With the revival of the textile industry and the steady growth of the pharmaceutical industry, there is an increase in the discharge of drug residues and dyes into wastewater. Dyes in wastewater have several effects. The presence of these dyes in wastewater may lead to the collapse of the Kenyan textile industry due to non-compliance with the quality standards set out in the ISO14000 certification. The collapse of these industries reduces countries' foreign income and undermines the achievement of the Big Four Agenda and largely Vision 2030.

Since most treatment of wastewater industries is not intended to remove pharmaceutical residues, the majority of them are discharged into bodies of water, posing a significant risk to aquatic life. Diclofenac, for example, has an endocrine-disrupting impact on fish eggs by delaying and lowering hatching success and, at low concentrations, harming the digestive organs, notably the gills. This has led to a decline in fish stocks in the lakes. Therefore, proper pretreatment of pharmaceutical wastewater is required to minimize contamination and ecosystem disruption. Photocatalysis is the most effective method for eliminating harmful contaminants from wastewater. Despite adsorption technology's relative cost, there is a important need in replacing expensive commercially available adsorbents such as activated carbon with less expensive alternatives. To solve the cost issues associated with expensive commercial adsorbents and the efficacy of adsorbents with low-cost, a nano-silica composite adsorbent was produced from agricultural waste.

1.3 Objectives of the Study

1.3.1 General Objective

To synthesize, characterize and use Irish potatoes peels powder/Nano silica composite (IPPP-NSC) in degradation of RB and DCF.

1.3.2 Specific Objectives

i. To synthesize IPPP-NSC composite.
ii. To determine the structural, and textural properties of the composite
iii. To assess the composite's effectiveness in degradation of RB dye and DCF

1.4 Research Questions

In this research we were seeking answers to the following questions

i. Can a composite from IPPP and nano silica be synthesized?
ii. How are the structural, and textural properties of the composite?
iii. How efficient is the IPPP-NSC in degrading RB dye and DCF?

1.5 Significance of the Study

Unclean water and inadequate sanitation and hygiene have contributed as much to about 1.8 million deaths each year due to water pollution-related diseases. Discharging dye-rich wastewater into natural water systems has a significant negative environmental impact since dyes are hazardous to aquatic and marine life and damage the aesthetics of the environment. There have been reports of adverse health consequences connected with the low levels of diclofenac in aquatic habitats. It has been linked to vulture population decreases in Asia. At a concentration of 1 μg/L, it is also known to influence organ histology and gene expression in fish. Industries suffer greater costs as a result of the usage of adsorption carbon since NEMA has put in place severe regulations and penalties to make sure that water discharged from industries is of an acceptable quality. In order to reduce treatment costs, development of cost-effective alternative adsorbents having adsorption capacity that is high.

Due to their effectiveness and environmentally friendly nature in adsorbing colors and drug residues from wastewater, biomaterials-based biosorbents have recently gained a lot of attention. However, biomaterials do not exhibit extremely good biosorption capability in their original state or without any modifications. Making composite materials can increase the effectiveness of these adsorbents. IPPs and rice husk are agricultural wastes and are locally available hence they can be exploited for removal of RB and DCF from waste water. Besides rice husk ash has high content of silica. In addition, IPPs contain starch which make it a good natural binder.

CHAPTER TWO

LITERATURE REVIEW

2.1 Water Pollution

The availability of clean water is essential for socioeconomic development and maintaining human health. This water should be safe and of high quality (Cosgrove *et al*., 2015). However, the quality of water has deteriorated due to the invention of new technologies, and population growth which has led to increasing discharge and detection of chemicals of concern at nanogram or microgram per liter levels (Khilchevskyi *et al*., 2021). This rapid growth has led to environmental problems, particularly pollution, with water pollution posing the greatest threat to humanity's sustainability.

Pollution of waters is defined as the change in the chemical, biological or physical features of water that is damaging to human health, survival, or activities (Meride *et al*., 2016). Water contaminants are classified into point sources and non-point sources. When contaminants enter a body of water directly, they are referred to as point sources. These include wastewater treatment plants; paper and pulp mills; oil refineries; factories, automotive and electronics manufacturers (Ritter *et al*., 2002). Nonpoint sources deliver water pollutants indirectly through environmental changes, such as when runoff from rain and snowmelt transport pollutants into waterways (Wato *et al.,* 2020).

2.2 Pharmaceuticals

Personal care and pharmaceutical products (PCPPs) are ubiquitous and have been identified as a possible environmental threat since the late 1990s (Hena *et al*., 2021). There are approximately 3500 pharmaceutical molecules listed in the global pharmacopoeia and over 10% of these chemicals have been found in aquatic settings (Dossey, 2010). Personal care items, pharmaceutical goods, surfactants, hormone disrupting substances, flame retardants, insecticides, and industrial preservatives are among the increasing pollutants (Varjani *et al*., 2018).

PCPPs are prevalent in the environment due to their harmful and tenacious potential for performance in high spectrum PCPPs, and they cannot be efficiently removed by typical treatment plants for wastewater (Kyzas *et al*., 2015). The release of waste from hospitals into municipal wastewater treatment plants (WWTP) lowers the biodegradation of organic contaminants (even at diluted medication doses). The constant addition of diclofenac to the oxygen-deprived muck treatment technique was found to diminish gas generation and the denitrification potential of the microbial community at the wastewater treatment plant. (Tiwari *et al.*, 2017).

Analgesics, diuretics, antibiotics, NSAIDs, antimicrobials, stimulants, cosmetics, antiseptics, nutritional supplements, sunscreens, and scents are examples of PCPPs (Ślósarczyk *et al.,* 2021). Ibuprofen, carbamazepine and diclofenac are the active pharmaceutical ingredients (PACs) detected in wastewater at the highest concentration because they are sold in the largest quantities (Ślósarczyk *et al.,* 2021). In fact, they have been measured and recorded in water samples from approximately 70% of the different countries where water samples were collected (Mailler *et al.,* 2015).

The pharmaceutical industry, hospitals, research operations, animal excrement containing target compounds, and the dumping of outdated pharmaceuticals or chemicals into the environment, are the primary sources of PCPPs in the environment (Mompelat *et al.,* 2009). Hospitals contribute significantly to pharmaceutical pollution in the environment. Drug residues and its metabolites, radioactive elements, drug conjugates, and other contaminants may be discharged into the environment as a result of veterinary PhACs manufacturing activities in metropolitan areas (Pereira *et al*., 2017).

Surface rivers can be contaminated by PCPPs from biosolids distributed on agricultural land, as well as irrigation from polluted water sources. Pollutants can contaminate groundwater through bank filtration or leaching in the latter scenario. Because sediment has binding sites of a wide range, it can adsorb PCPPs both inside the surface water compartment and by irrigation with PCPP-containing treated or untreated effluent (Wang and Wang, 2016). This has the potential to impact water quality, drinking water supplies, ecosystems, and human health.

2.3 Environmental Impacts of Pharmaceuticals

PCPPs in environment that they reach have negative impacts on aquatic life and constitute a danger to human health (Sengar *et al*., 2022). These compounds, which can be hazardous and bioaccumulate, have been recognized as impending organic pollutants (Mijangos *et al*., 2018). Often bioaccumulation is linked with a compound's high lipid solubility and capacity to accumulate in live creatures' fatty tissue over time. As these persistent compounds move in within the food chains and accumulate due to digestion and degradation in particular organ tissues, they become more harmful to the environment (Venegas *et al.,* 2021).

Recent research investigations into toxicity have indicated that while low concentration molecules of pharmaceuticals have no acutely detrimental effects on aquatic creatures, their continual exposure and release to aquatic life may have consequences in the long-term (Tiwari *et al*., 2017). Aquatic toxicity, development of disease resistance and genotoxicity are among the impacts (Prajwal *et al*., 2017). As a result of mussel and mussel DNA modifications, these effects include damage to fish digestive glands and poor male reproductive health. Other laboratory investigations have shown that when zebrafish were subjected to treated effluent for 7 days, egg yield was reduced by 50% (Cuevas *et al*., 2015)

Long-term exposure could reduce the population of vultures. A research in Asia found that consuming the veterinary medication diclofenac induced renal failure and visceral gout (Tiwari *et al*., 2017). This group's vast variety of chemical classes generalizes about their adverse environmental behavior. Given the high frequency of cancer in the community, one example is the impact of chemotherapy medication discharge into the environment (Johnson *et al*., 2008).

Acute or chronic poisoning, endocrine disturbance (interference and detoxifying systems that drive reproductive processes), and primary productivity inhibition are all possible environmental consequences (Jaishankar *et al*., 2014). PCPPs are also hazardous to the food chain as they affect the aquatic environment nitrification process due to the sensitivity of nitrosomes and Nitrobacter bacteria to oxytetracycline. Carbamazepine, diclofenac, and metoprolol have been found in studies to produce cellular alterations in numerous organs of rainbow trout at low dosages up to 1000 ng/L (Opanga, 2018). Some of the PCPPs included:

(a) Triclosan (TCS)

Triclosan is an aromatic phenol ether having chlorine group at C-5 and 2,4-dichlorophenoxy group at C-2. Its chemical formula is $C_{12}H_7C_{l3}O_2$, as shown in Figure 1(Thomaidi *et al.*, 2017). It is employed in PCPPs as an antibacterial agent as well as a disruptor of the endocrine system. It may interact with chlorine in water to generate carcinogenic chloroform. It’s also a cause of concern for scientific and regulatory communities, particularly in Western countries (Dhillon *et al.*, 2015). On January 27, 2016, the European Union (EU) prohibited it’s use in biocidal products due to the unacceptable environmental risk (Thomaidi *et al.*, 2017).

After September 2, 2016, OTC consumer antiseptic detergents with TCS were not allowed to be advertised in the United States (Iacopetta *et al.*, 2021). TCS, an antimicrobial ingredient, is now present in numerous items such as soaps, toothpaste, home cleansers, and fabrics like clothing, bedding, shoes, and carpets. TCS content in these items was found to be in the 0.10.3 wt% range. TCS values between 9 ng/L and 6.7 g/L were found in wastewater (Chalew *et al.*, 2009).

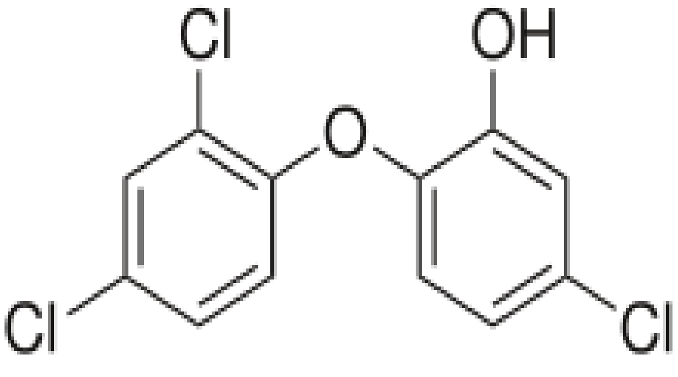


Figure 1. Triclosan

(b) Carbamazepine (CBZ)

Carbamazepine is a dibenzoazepine, i.e. 5H-dibenzoazepine, which carries a carbamoyl substituent on the azepine nitrogen with the molecular formula $C_{15}H_{12}N_2O$ as shown in Figure 2 (Nieto-Juárez *et al.*, 2021). It is an antiepileptic medication that is used as psychic energizer. It is ubiquitous in urban wastewater, and due to its chemical stability, traditional biological treatment does not efficiently remove it (Nieto-Juárez *et al.*, 2021). As a result, it was determined that it was a recalcitrant medication dumped into surface waterways with secondary effluents (Baena-Nogueras *et al.,* 2017).

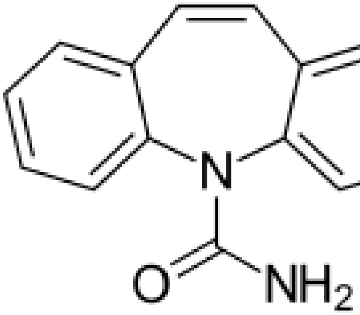


Figure 2. Carbamazepine

(c) Caffeine

It is a methylxanthine alkaloid consisting of bicyclic molecules originating from the purine ring system (Amaresh *et al.,* 2011). Its molecular formula is $C_8H_{10}N_4O_2.H_2O$ with its chemical structure shown in Figure 3. Caffeine sources are tea, coffee, soft drinks and energy drinks. It has a stimulant effect and as a result, it is commonly identified in high amounts in raw sewage (Weinberg *et al.*, 2004). Because of its ubiquitous occurrence in the aquatic environment, CAF is as an emerging organic pollutant. (Tang *et al.,* 2020).

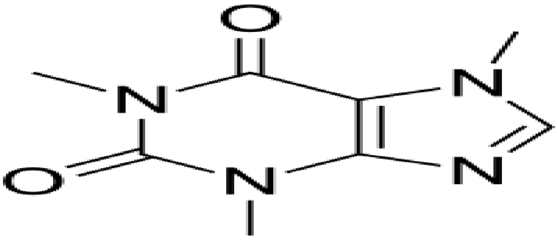


Figure 3. Caffeine

(d **Diclofenac**

It’s nonsteroidal anti-inflammatory drug with a molecular formula ($C_{14}H_{10}C_{l2}NNaO_2$) and a chemical structure shown in Figure 4, which is used widely in the treatment of inflammatory diseases and pain (Parolini 2020). It’s commonly found in water for drinking at concentrations less than 10 ngL^{-1} (Osorio *et al.*, 2022). DCF was identified as a priority chemical for monitoring in the EU Water Framework Directive in 2015 (Gonzalez-Rey *et al.*, 2015). Despite modest doses, DCF has been shown in studies to have impacts on a variety of species, and it has great acute toxicity to aquatic species among the anti-inflammatory medications (Parolini 2020). DCF values in wastewater treatment plant the effluent can range from zero and 269 ng/L (Salvestrini *et al.*, 2020).

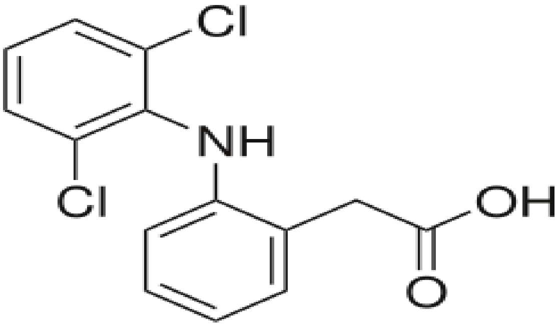


Figure 4. Diclofenac

(e) **Naproxen (NAP)**

It's a methoxynaphthalene with a carboxy ethyl group at C-6. It has a chemical structure as shown in Figure 5 and a molecular formula of $C_{14}H_{14}O_3$ (Chander *et al.*, 2011). It is used to relieve fever, pain, and stiffness caused by conditions such as psoriatic arthritis, kidney stones, osteoarthritis, gout, primary bursitis Dysmenorrhea, tendonitis, and menstrual cramps. Continuous NAP discharge into the aquatic environment might endanger non-target creatures (Hanafiah *et al.*, 2022). The high detection NAP levels in natural waterways are attributable to wastewater treatment techniques' inadequate degrading effectiveness. The concentrations of NAP in wastewater treatment plant influents generally vary from 8.84 to 16.17 ng/L (Santos *et al.*, 2013).

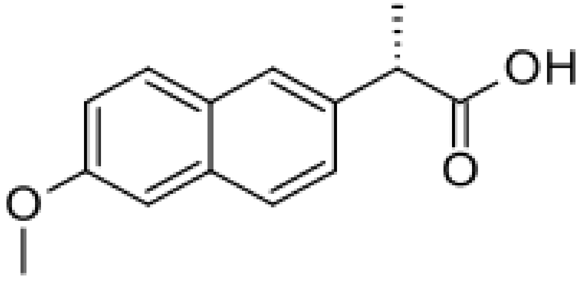


Figure 5. Naproxen

(f) **Ketoprofen (KET)**

It is monocarboxylic acid, which is made of propionic acid and a 3-benzoylphenyl group at position 2, having molecular formula $C_{16}H_{14}O_3$ and has chemical structure shown in figure 6 (Syed 2019). It is widely used in medical care due to its ability to treat musculoskeletal injuries and inflammatory diseases (Zunngu *et al.*, 2017). Since huge amount of ketoprofen taken by people, it's frequently discovered in wastewater and surface water with other NSAIDs. KET concentrations in wastewater treatment plant influents generally vary between 289 and 589 ng/L (Santos *et al.*, 2013).

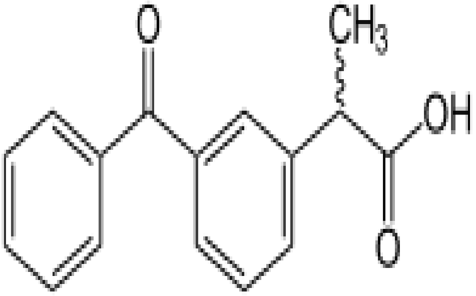


Figure 6. Ketoprofen

(g) Methyl Paraben (MPB)

Methylparaben ($CH_3(C_6H_4(OH)COO)$, is a p-hydroxybenzoic acid methyl ester, and has structural formula as shown in Figure 7 (Dobrin *et al.*, 2014). It's frequently utilized as an antibacterial agent in pharmaceuticals, cosmetics, and toiletries. The Cosmetics Directive has banned or limited the use of MPB (Bailey, 2017). Recently, methylparaben-free labeling have appeared on cosmetic goods (Steter *et al.,* 2016). MPB concentrations in wastewater inflows averaged 6.4 mgl^{-1} (Haman *et al.*, 2015).

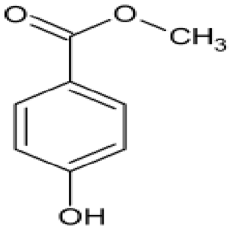


Figure 7. Methyl Paraben

2.4 Removal of Pharmaceuticals Residues from Water

Pharmaceutical residues have been eliminated from waste water using a variety of techniques. According to Castiglioni *et al.*, (2006), these include adsorption, electrochemical degradation, photocatalytic degradation, oxidation, nanofiltration, and membrane filtration. Activated sludge (Clara *et al.*, 2005), membrane bioreactor, conventional treatment, heterogeneous catalytic oxidation with H_2O_2, solar irradiation, granular activated carbon, ultrafiltration, coagulation/flocculation, and the process of reverse osmosis have been used to remove DCF from waste water. Because of its simplicity, adsorption has an advantage over other approaches. with a mud-free environment, and may entail a low-cost investment in terms of both acquisition costs and necessary area. Although activated carbon is quite good at eliminating contaminants, it is very expensive to create. Agricultural byproducts, industrial byproducts, clay, and other low-cost adsorbents have all been produced (Sannino *et al.*, 2012).

2.5 Dyes and their Effects on Human

Humans rely on natural resources such as air, food, and water for survival. Water covers More than 70% of the earth's surface is covered with water. However, much of this water is unsuitable for human consumption. Fresh water is already very scarce in many regions of the world (Schwarzenbach *et al.*, 2010). As the population rises and climate change takes effect, it will become much more limited. This limitation is brought about not just by growing water demand, but also by contamination of freshwater environments. Pollution decreases the availability of suitable industrial water and the pollution increases cleaning costs. Organic and inorganic contaminants are the most prevalent in water. Because most industrial operations take place near bodies of water, they are being more contaminated by organic and inorganic contaminants. Potential pollutants have an impact on human health as well as industrial or agricultural water consumption. (Schwarzenbach *et al.*, 2010).

Dyeing wastewater from sectors such as leather, paper, pulp, and food is difficult to treat, not only because to its chemical oxygen demand which is very high, but, also because paint is the first pollutant apparently visible to the naked eye (Pandey *et al.*, 2007). Untreated industrial wastewater poses great dangers to the environment because its chemical structure makes it stubborn and unruly. Non-biodegradable organic and inorganic compounds in textile wastewater include paints, phosphates, metals, aerosols, high BOD and COD concentrations, phenols and surfactants (Sahu *et al.*, 2014).

A dye is a colored substance applied to textiles and frequently used in solution. Good quality dye must be 'fast' or stable chemically, thus it does not wash away with washing and water or start fading when exposed to sunlight (Khatri *et al*., 2015). It's a molecule made up of two major components: auxochromes, which makes the molecule soluble in water and possess a stronger affinity for fibers, and chromophores, which are responsible for color. Metals, aromatics, and other substances included in dyes may influence photosynthetic activity of aquatic life and may be harmful to some aquatic organisms (Ali *et al*., 2009). Because of their harmful consequences, dyes have sparked widespread concern about their use. It has been linked to cancer, mutagenesis, respiratory damage and chromosomal breakage. The structure is more intricate and stable, making dismantling the printing and dyeing wastes more difficult (Pandey *et al*., 2007). Some dye qualities are determined by their application and can be roughly classed as follows:

(a) Basic Dyes

As auxochromes, basic dyes include amino or alkylamino groups and are thus positively charged overall, reacting with negatively charged compounds (Rajesh *et al.,* 2014). They are formed by the reaction of aromatic bases with acids. They are colorful organic base salts with amino groups as their basic groups, which dissolve in water and dissociate into colored cations and acid anions. Because the dyes have a positive overall charge, they are also known as cationic dyes (Velusamy *et al*., 2021). They are the most vibrant and bright of the known, synthetic dyes, but possess poor light and wash fastness, such as Rhodamine Blue, which has the chemical formula $C_{28}H_{31}ClN_2O$ and the structural formula given in Figure 8 (Garg, 2012).

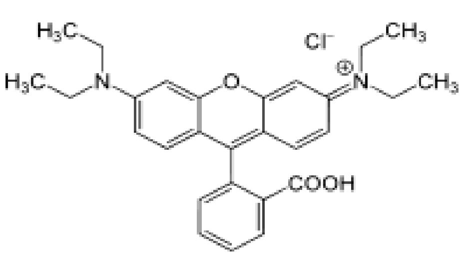


Figure 8. Rhodamine Blue

(b) Acid Dyes

When an ionic bond is created inbetween the protonated -NH_2 group of the fiber and the acidic group of the dye, a sulfonic, carboxylic or phenol organic acid sodium salt is generated (Marras, 2015). Colored anions are fixed in the dyed material due to ionic interaction with fibre cationic sites during dyeing (Bensalah, 2020). Acid dyes are water soluble due to the sulfo or carboxy group on the molecule. It is theorized that, Van der Waals forces, hydrogen bonding and ionic interactions hold them to threads. Because the dyes are often sold as sodium salts, they are usually anionic in solution (Li *et al*., 2019). Acid Yellow 36 is an example of a member of the class.

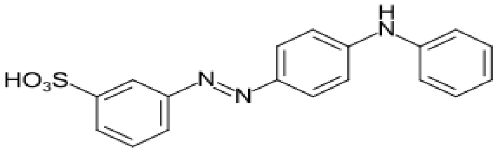


Figure 9. Acid Yellow 36

(c) Direct Dyes

Direct dyes refer to a class of colored, water-soluble compounds that have an affinity for fiber and are absorbed directly, such as direct orange 26, as shown in Figure 10 (Choudhury, 2018). They may be applied to textiles immediately from an aqueous solution. They are ideal for fabric coloring because they can create hydrogen bonds. Their colors are not vivid as the basic dyes, but are more resistant to light and washing, and this resistance may be improved further by post-treatments (Tripathi and Rai, 2022). They typically have a large molecular weight and an N=N azo bond. Because of their sulfonic acid groups, they are water soluble. An example of a direct dye is Direct orange 26.

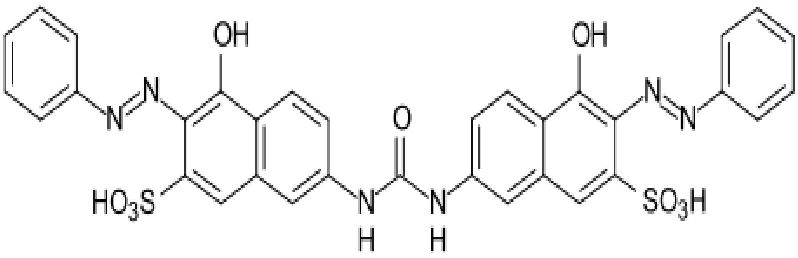


Figure 10. Direct orange 26

(d) Disperse Dyes

To begin, secondary cellulose acetate strands were colored using dispersion dyes. Because they are water insoluble, they are colored by grinding them into a fine powder and dispersing them (Koh, 2011). In the dye bath, a dispersion of dye particle suspension generates a very dilute dye solution, which are then absorbed by the fibers. These non-ionic dyes are very insoluble (Kayranli 2011). Figure 11 shows a nice example of a dispersion dye, dispersion Red 11.

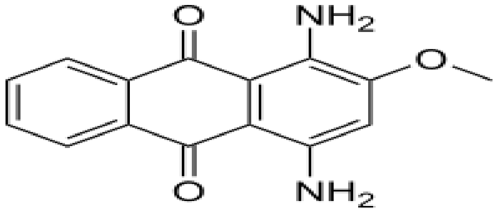


Figure 11. Disperse Red 11

(e) Sulphur Dyes

These are really deep colors with good washing resistance but poor sun resistance. Cotton, linen, and rayon will all be coloured, albeit subtly (Jain and Jain, 2020). Sulphur dyes, on the other hand, have a disadvantage of making the fabric structure delicate or weak, causing it to break readily. Sulfur dyes are applied to cotton after an alkaline reducing bath in which sodium sulfide is used as a reducing agent. They are inexpensive and have excellent resistance to light, washing, and acid. Cotton and rayon are its primary applications (Katheresan *et al*., 2018). An example is sulfur red 7 (Figure 12).

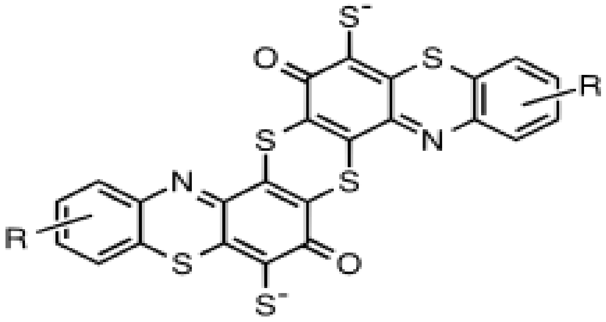


Figure 12. Structure of Sulfur red 7

(f) Reactive Dyes

These pigments covalently link with cellulose fibers. Which results in colorful fabric which have excellent wash fastness. The textiles dyed with a reactive group, directly interacts with the hydroxyl or amino group of the fiber (Khatri *et al.*, 2015). They contain a chromophore linked to a substituent that can interact with the fiber substrate directly. The covalent connection, connecing reactive dyes to natural fibers is the primary reason they are categorised as permanent hues. Cotton, nylon and wool are among the materials utilized. The color arises immediately and lasts for a long time due to the chemical reaction (Faisal, 2013). Dichlorotriazine dye, depicted in Figure 13, is an example of this type.

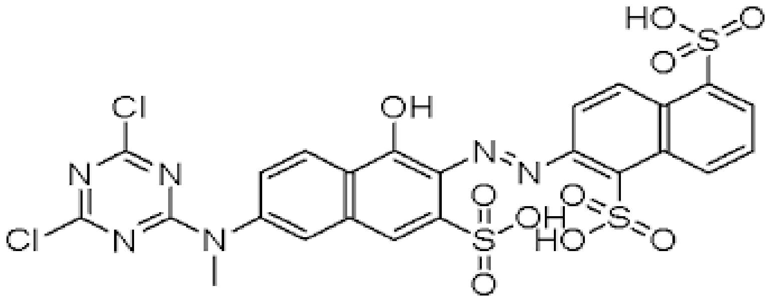


Figure 13. Dichlorotriazine

(g) Solvent Dyes

Alcohols, liquid ammonia, and chlorinated hydrocarbons are soluble in the aforementioned colors, but not water. These colors dissolve in the target lipid or a non-polar solvent. This is used as a categorizing and naming approach in the Color Index. They are responsible for the color of synthetics, polymers, fuels, oils, and waxes (Tian *et al.*, 2020). Used in the production of polymers, fuels, lubricants, and oils, among other things. One example is solvent red16 shown in Figure 14.

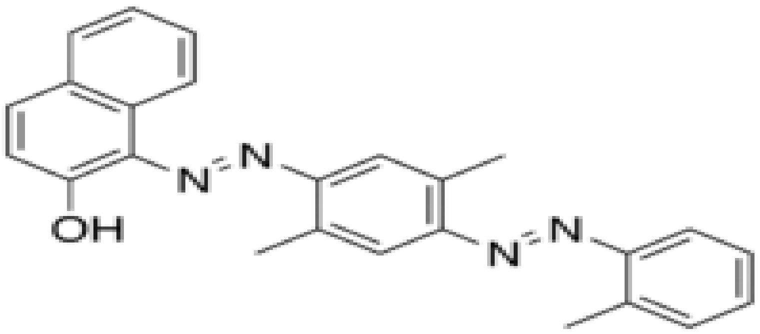


Figure 14. Solvent red 16

(h) Vat Dyes

These are complicated polycyclic compounds with a quinone structure that are insoluble and incapable of directly coloring textiles. The reduction in alkaline liquor yields water-soluble dye alkali metal salt, which in this form has a high affinity for the textile fiber (Morin, 2017). The term vat originated from an old indigo dyeing method that involves the reduction of indigo to a light condition. Vat dyes are made from indigo, carbazole, and anthraquinone. The dyes are capable of working with wool, cotton, linen, silk, rayon, and, in rare occasions, nylon. They are also used in continuous application of pigments throughout the dyeing process (Jain & Jain, 2020).

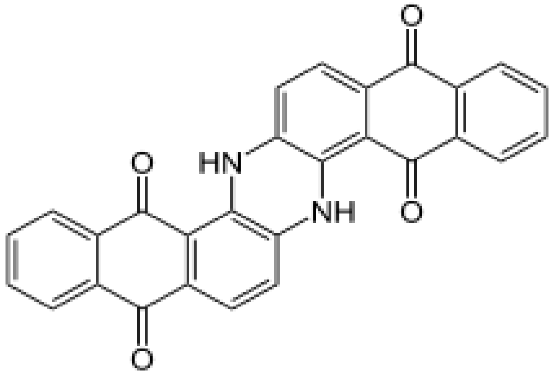


Figure 15. Vat Blue 4 (Indanthrene)

2.6 Removal Techniques of Dyes

The eradication of dyes from effluent is a serious issue in the subject of water pollution, which poses a huge environmental catastrophe. To remove colours from wastewater, many treatment procedures are available (Zekker, 2022). To remove colours from industrial effluent, many chemical, physical, and biological processes are often utilized. Oxidative reactions, H_2O_2-Fe(II) salts and ozonation, , sodium hypochloride, photochemical, cucurbituril, and electrochemical destruction are examples of chemical techniques (Singh and Arora, 2011). Adsorption, ion exchange, membrane filtration, irradiation, and electrokinetic coagulation are all physical dye removal procedures. Due to high costs and sludge disposal issues, many traditional dye wastewater treatment procedures have not been widely adopted in large-scale enterprises (Crini, 2006).

2.6.1 Biological Methods

When microbial biocatalysts for dye removal in textile wastewater provide potential advantages over traditional procedures due to minimum environmental impact and cost-effectiveness (Maeda *et al.,* 2002), treatment is often the most cost-effective option. These procedures do not require strict supervision and produce non-toxic final products. Stolz (2001) suggests that this process might be aerobic, anaerobic, or a mix of the two. Bacteria, algae and fungi are the microorganism families that have garnered the most attention in these techniques for their ability to detoxify colored effluent. Dead cells that adsorb dyes are separated from living cells that biosorb and degrade dyes (Fu and Viraraghavan, 2001). The fundamental step in mineralizing synthetic lignin or dyes is the biodegradation of live cells, which can produce lignin peroxidase. manganese peroxidase, lignin-modifying enzyme laccase. Biosorption, involving physicochemical interactions like ion exchange, deposition, and adsorption, is the mechanism for dead cells (Wesenberg *et al.*, 2003).

2.6.2 Chemical Methods

These include flocculation, electrokinetic coagulation, electro-flotation, precipitation-flocculation with $Fe^{2+}Ca(OH)_2$, and irradiation (Mukherjee *et al.*, 2013). These chemical procedures are useful in removing dyes and herbicides from wastewater, but they are expensive and thus rarely employed, and they have the disadvantage of posing a disposal challenge due to the formation of concentrated sludge. These technologies are effective for treating polluted waste water, but they are not generally used due to issues such as high electrical energy consumption, chemical reagent use, and expense (Shannon *et al.*, 2010). To remove dyes, oxidizing chemicals like hydrogen peroxide, ozone, and permanganate are used. However, these oxidizing agents produce hazardous disinfection by-products (Malato *et al.*, 2009).

2.6.3 Physical Methods

A typical process of treatment is a series of procedures, with the output of one becoming the input of the subsequent one. The first phase is frequently made up of physical processes. A variety of physical treatments are applied, including membrane-filtration technology and other adsorption techniques (Van der Bruggen *et al.*, 2003).

2.6.3.1 Membrane Separation Processes

Ultrafiltration, microfiltration, reverse osmosis, and nanofiltration, which are based on membrane pressure, are often used for dyeing wastewater treatment (Van der Bruggen *et al.*, 2003). It has several advantages, including low energy consumption, high separation efficiency, low pollution, and easy operation. The membrane is used in wastewater treatment to filter and separate colors and pollutants. However, due to the restrictions of requiring specialized equipment, expensive investment, and membrane fouling, among other factors, this approach is still not frequently used (Jamaly *et al*., 2014).

2.6.3.2 Adsorption Techniques

The buildup of a liquid or gas solute results in the creation of a molecular or atomic film on a solid or liquid surface. The adherence of atoms, ions, biomolecules, liquids, or dissolved solids to a surface leads in the creation of an adsorbate layer on the adsorbent surface. The adsorbent is the binding material. Because the atoms on the adsorbent's surface aren't completely covered by other atoms, they can attract adsorbates. It might be chemical or physical (Cornelissen *et al*., 2005).

Adsorption capacity is determined by the chemical and physical characteristics of both the adsorbate and the adsorbent, as well as the solution concentration of the adsorbate in liquid, experimental circumstances including temperature, contact duration, and pH (El Qada et al., 2008). Adsorption mostly takes place on the pores walls or at particular spots inside the particle. Because holes are frequently tiny, the surface area inside is greater than the outer surface area. Because of variances in shape, molecular weight, or polarity, certain molecules adhere to the surface more strongly than others. The adsorbate is typically kept strong enough to allow the component to be completely removed from the solution. Several adsorbents materials have been investigated as wastewater treatment adsorbents. Silica gel, zeolites, activated aluminum oxide, and activated carbon are among the most important (Crini *et al.*, 2019).

2.6.3.2.1 The Silica Gel

It is manufactured by reducing the pH of a solution of alkali silicate to less than ten. It is environmentally safe, inert, and reliable. Because of the large number of immobilized organic molecules in silica gel, it has a high metal ion sorption capacity (Rangsayatorn *et al*., 2004). Several investigations looked into the basic dyes' adsorption on silica; while the capacities of adsorption were strong, however, silica is an expensive as an adsorbent (Gupta *et al*., 2009).

2.6.3.2.2 Zeolites

Natural zeolites are plentiful low-cost resources because they are hydrated crystalline aluminosilicates containing holes inhabited by alkali water, and alkaline earth cations (Wang and Peng, 2010). Malachite Green was recovered in batch mode from aqueous solution using natural zeolite and reused using microwave radiation. The regeneration yield was 85.8 percent after 10 minutes of microwave irradiation at 160 W, and the adsorption capacity at 308 K was 25.14 mg/g (Han *et al.*, 2010).

2.6.3.2.3 Activated Alumina

It is composed of many of partially hydroxylated alumina oxide in non-equilibrium forms. It is a porous and absorbent filter material created by processing aluminum ore. The fundamental drawback of activated alumina, is its highest adsorption effectiveness at low pH levels, and contaminants such as arsenites must be oxidized to arsenates before adsorption process. Several treatment techniques would be necessary to reduce levels of additional health-related contaminants (Johnson and Bouchard, 2005).

2.6.3.2.4 Activated Carbon

Despite the fact that this is the most widely used and popular adsorbent in wastewater treatment, researchers are actively looking for cost-effective adsorbents for water pollution treatment where cost is a consideration (Crini, 2006). Adsorbents with a low cost can be manufactured from a range of abundant and low-cost raw materials with a organic content and a low inorganic content that are easily activated. Benefits of making cost-effective adsorbents from waste materials or materials of little use, are several, the most important of which are economic and environmental (Bhatnagar and Sillanpää, 2010).

2.6.3.2.5 Agricultural Wastes

Making wastewater adsorbents out of locally accessible and cheap materials like agricultural waste and industrial leftovers may assist to minimize waste disposal expenses while also providing a cheap alternative to commercially supplied activated carbon (Kurniawan *et al*., 2006). Because of their environmentally favorable and cost-effective character, chemical composition, and renewable nature, agricultural waste products are a viable alternative for wastewater treatment (Acharya *et al*., 2018).

(a) Rice and Wheat Waste Adsorbents

Rice is the world's most significant staple food and a vital commodity grown worldwide. Rice husk is a rice business byproduct, used to create low-cost adsorbents for the removal of dyes and heavy metals from wastewater. It is an effective adsorbent for dyes removal from wastewater, such as Malachite Green, Reactive Orange 16, and Acid Yellow 36 (Safa and Bhatti, 2011). Wheat is another important staple crop that produces byproducts like wheat bran and wheat husk. The dye adsorption by wheat bran was studied by (Choudhary *et al.*, 2007).

(b) Agricultural Waste Peels

The outer protective covering of a fruits or vegetables are becoming popular as a wastewater treatment adsorbent. As low-cost adsorbents, cassava, banana, orange, mango, and pine apple peels were used to remove color from wastewater. The agitation period, starting dye concentration, adsorbent dose, and pH on the effectiveness of adsorption of Direct Blue 86, Rhodamine blue, Acid Violet and Congo Red by orange peel were studied (Patel, 2012) investigated the usage of lemon peels as adsorbent for Malachite Green removal.

(c) Nano Silica

The science of molding and creating macro atoms into nanomaterials is known as nanotechnology. Inorganic nanomaterials are becoming increasingly attractive because to their distinct and size-related physiochemical properties in compared to bulk matter. Because of their novel properties, nanomaterials have been used in a wide applications range, including cosmetics, medicine, renewable energy, catalysis, and biomedical devices (Albrecht *et al.*, 2006). According to study, the sodium silicate nano adsorbent is a good adsorbent for dye removal and may be useful in other areas of environmental research. There has been little investigation into the use of nanosilica for color and pharmaceutical residue degradation.

2.6.3.2.6 Composite Based Adsorbent

Several efforts have been made to effectively create an outstanding adsorbent for various types of pollutant removal in aqueous or real effluent, with the emphasis being placed on the synthesis of an adsorption material that integrates the distinct characteristics of a specific adsorbent with other substances such as bentonite, fly ash, zeolite chitosan, polymer isomers, and montmorillonite (Leboda *et al*., 2006). The goal of the composite adsorbent is to maximize pollutant absorption in textile wastewater by combining strong hydrophilic and hydrophobic characteristics with better mechanical robustness and chemical resistance. However, these materials need significant modification and shaping for laboratory and commercial applications (Leboda *et al*., 2006). As a result, the utilization of various minerals has demonstrated that combining mineral and carbon materials to create complex sorbents and hybrid materials is possible (Szychowski and Pacewska, 2012). Because of its mosaic nature and adsorption capacity for both inorganic and organic molecules, mineral carbon-based adsorbents are in great demand (Leboda *et al*., 2006).

The adsorbents composed of carbon-mineral was initially explained by Leboda (1992). According to the executive summary of his study, manufacturing procedures might include mechanical mixing, integration, carburization, and carbon deposition on catalyst and adsorbent surfaces throughout different adsorption and catalysis processes. Organic compounds that are chemically or physically bound to the mineral adsorbent's surface can also be carburized. Following that, the authors began investigating and testing several precursors for the development of composite-based adsorbents (Putyera *et al*., 1994) used nitrogen adsorption isotherms and inverse gas chromatography to evaluate the properties of adsorption of montmorillonite and hydrotalcite matrices. They discovered that hydrotalcite has a greater adsorption capacity per unit mass than montmorillonite-based materials.

Another work (Yanagisawa et al., 2010) studied removal of heavy metal ions from water using a combination of activated carbon made from coconut shells and magnesium. They discovered that the magnesium composite absorbed more Cd^{2+} and Zn^{2+} ions than a comparable material. Additionally, it was discovered that loaded magnesium was most likely coupled to the carbon surface through an oxygen bridge. Ai and Jiang (2010) examined the rapid dye removal with an AC/Ferrospinel composite. Methyl Orange (MO) and Basif Fuchsin (BF) adsorption capabilities were determined to be 95.8 and 101.0 mg/g, respectively, and to follow the Langmuir model.

Sandeman *et al*., (2011) used PVA hydrogels, activated carbon, and a PVA/AC hybrid to remove cationic dyes including methylene blue, methyl orange, and Congo red from water. The interactions with PVA/AC composites were shown to be reliant on the dyes' symmetry, charge sign, size, and value, as well as the type of AC or PVA/AC surface available for adsorption, as well as textural and structural features (Yang *et al*., 2008). The maximum adsorption capacity of magnetic Fe_3O_4-activated carbon produced from rice husk against aqueous Methylene Blue (MB) was 321 mg/g, the composite had a reasonably broad pore width of 3.1 nm and 770 m^2/g surface area.

A magnetic cellulose/Fe_3O_4/activated carbon composite due gave the highest elimination of Congo red from aqueous solutions due to the superparamagnetism phenomena (Zhu *et al*., 2011a). Singh et al. (2011) created a magnetic carbon-iron oxide from coconut shell. The optimal conditions, according to the Langmuir model, were a temperature 50°C, pH 8.5, concentration of 240 mg/l, and a dose 1g/l, with the maximal adsorption capacities of crystal violet reaching 81.70 mg/g. While there are several methods for converting various precursors into composite-based materials, many researchers remains optimistic of the benefits of composite materials due to the tremendous advantages it may provide for adsorption in liquid-phase systems.

2.7 Adsorption Isotherms

They are mathematical equations showing the relationship between the amount of adsorbate which is adsorbed on an adsorbent and the concentration of adsorbate in solution on attaining equilibrium at a fixed temperature (Abin-Bazaine et al., 2022). Adsorption isotherms are produced by studying a volume-determined solution containing a certain quantity of adsorbate solution as well as various adsorbent doses (De Souza *et al*., 2021) agitate the mixture at a steady temperature until equilibrium is achieved. When this occurs, the concentration of the adsorbate in the aqueous phase is recorded, and the adsorption capacity at equilibrium is estimated for each experiment using mass balance. Because they characterize the mechanism of adsorption and assist in improving the adsorption process, two isothermal models, Langmuir and Freundlich, were used to emphasize the link between adsorption capacity and type of adsorption for an adsorbate-adsorbent system (Al-Wasidi *et al*., 2021).

2.7.1 Langmuir Isotherm Model

It gives the relationship of the molecule adsorption on a solid surface to gas pressure or medium concentration above the solid surface at constant temperature. The predication is on the assumption that of monolayer adsorption. Adsorption occurs at homogeneous adsorbent sites, according to Langmuir (Hameed, 2009). The correlation coefficients (R^2) are used to assess the applicability of the isotherm equation. The Langmuir isothermal models are depicted in Equation 1.

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{K_L q_{max}} \text{.. Equation 1}$$

where Ce is the equilibrium concentration of RB dye/DCF in solution, qe is the equilibrium concentration of RB dye/DCF on the adsorbent, and qmax is the monolayer adsorption capacity of the adsorbent. The sign KL represents the Langmuir adsorption constant. A straight line having an intercept of 1/qmax and a slope of 1/qo. KL may be calculated by graphing Ce/qe vs Ce. The favorability of the adsorption process was further proven by computing the dimensionless equilibrium parameter (RL), which is provided in equation 2.

$$RL = \frac{1}{1+K_L C_O} \text{ .... Equation 2}$$

Where C_0 represents the original dye/DCF concentration in solution. If the RL value is between 0 and 1, the process of adsorption is said favorable.

2.7.2 Freundlich Isotherm Model

It is an adsorption isotherm that relates the adsorbent's surface solute concentration to the solute concentration in the liquid phase with which it comes into contact. This model is based on a non-uniform heat of adsorption distribution over a heterogeneous adsorbent surface (Thirunavukkarasu and Nithya, 2020). The Freundlich isotherm was represented by Equation 3.

$$log\, qe = \frac{1}{n} log\, ce + log\, K_F \text{ .... Equation 3}$$

where Ce is the adsorbate's equilibrium concentration (RB/DCF), qe is the quantity adsorbed at equilibrium, KF is the Freundlich constant connected with adsorption capacity, and n is the adsorption intensity constant linked with heterogeneity factor. When log qe is plotted against log Ce, a linear graph should result, with the slope and intercept of the curve determining the values of n and KF, respectively. A larger n value suggests that the adsorbate and adsorbent have a stronger connection.

2.8 Adsorption Kinetic Study

The mass transfer and surface reactions of the adsorbent particles from the solution influence adsorption kinetics, during which external or intraparticle diffusion may take place (Oyekanmi *et al*., 2019). For the case of porous surface adsorption equilibrium, a mass transfer barrier typically prevents solute mass transfer to the site of adsorption (Saini *et al*., 2019). To get the optimal conditions for the entire batch experiment, the removal of RB and DCF, as well as their degradation at the equilibrium contact time, must be explored. Both kinetic models of pseudo first and pseudo second order are extensively employed (Kowanga *et al*., 2016).

2.8.1 Pseudo-First-Order

It is predicated on the number of unoccupied sites and considers diffusion to be the rate limiting step (Cai *et al*., 2017). Equation 4 gives its linearized expression (Yousefi *et al*., 2018).

$$\ln(\mathrm{qe}-\mathrm{qt}) = \ln\mathrm{qe} - \frac{\mathrm{k}_1}{2.303}\mathrm{t} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{Equation 4}$$

where qt is the quantity of adsorbed dye/DCF at time (t) and k1 represents the pseudo-first-order rate constant (Soldatkina and Zavrichko, 2019). Plotting a graph of ln (qe-qt) against time (t) yields the values of k1 and qe.

2.8.2 Pseudo-Second-Order

Chemisorption is the rate-determining phase in this model (Baby *et al*., 2019). Equation 5 depicts the linearized form.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{Equation 5}$$

where k2 indicates the pseudo-second-order rate constant (He *et al.*, 2019). The values of qe and k2 are obtained by plotting t/qt against time (t).

2.9 Analytical Techniques

2.9.1 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy is one of two vibrational spectroscopy methods often used in industry (the other being Raman). According to Tuck *et al.*, 2020, FTIR provides quantitative, qualitative, semi-quantitative, and information on physical characteristics and. chemical compositions It is possible to analyze solid, liquid, or gas materials in bulk or thin-film form. There are accessories available for examining the properties of materials at different temperatures. The aging and oxidation of asphalt binders, the identification and quantification of polymers in polymer-modified asphalt, the identification of concrete constituent phases, the analysis of pozzollons in concrete, and the analysis of alkali content in concrete are some examples of paving materials characterization. (Mazumder *et al.*, 2018).

2.9.2 Working Principle of FTIR

In an FTIR system, a burning black-body source produces an IR irradiation beam. The beam is subsequently sent and spectral encoding takes place in the interferometer. of Beams recombination with differing path lengths creates constructive and destructive interference, in an interferometer, which is referred to as an interferogram (Undavalli *et al.*, 2021). The beam now enters the sample compartment, where the sample absorbs the interferogram-specified frequencies of radiation. The sample is detected by the detector which detects the interferogram signal in energy versus time for all frequencies at the same time. Meanwhile, a reference (background) beam is superimposed for instrument operation (Undavalli *et al.*, 2021).

The spectrum required is obtained when Fourier transformation computer software is done to automatically remove the sample spectrum from the background spectrum. FTIR is used to investigate the twisting, bending, turning, and vibration of chemical bonds. If Io denote the intensity of incident infrared radiation and I denote the beam intensity after it interacts with the sample (Springfield, 2011). The ratio of intensities I/Io vs. light frequency yields a spectrum that may be expressed in three ways: reflectance, transmittance, and absorbance. The occurrence of numerous vibrations at the same time results in an extraordinarily absorption spectrum which is complex, which is an attribute of the functional groups that comprise the molecule as well as the atom arrangement. After interacting with the material, the detector measures the intensity of light (Ţucureanu *et al.*, 2016). Figure 16 shows a basic component in FTIR.

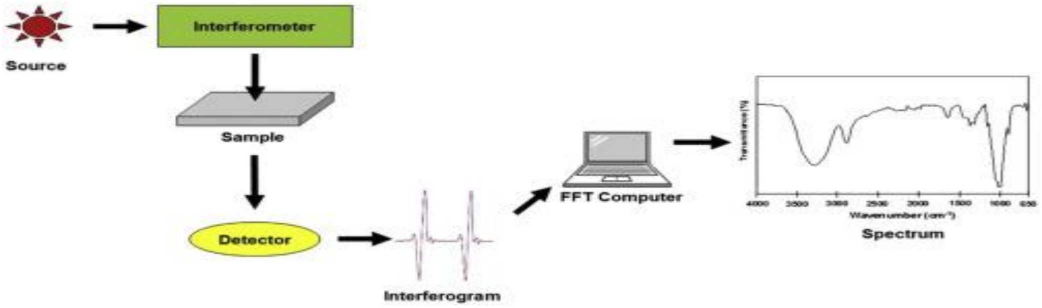


Figure 16. The basic components in FTIR spectrometer (Undavalli *et al.*, 2021)

2.9.3 X-ray Fluorescence Spectroscopy

It is used to identify both qualitative and quantitative chemical components in a sample. XRF is based on the emission of energy from an atom. When an electron in an inner shell is irradiated, an electron in a higher shell falls into the resulting "hole" and energy gets released equal to the difference in energy levels (Lodeiro *et al.*, 2009). This energy is emitted as an x-ray, with a wavelength specific to the element that emits it; this is the characteristic x-ray.

The material must be attacked with x-rays to separate the electron from the inner shell. An x-ray tube is used for this. X-ray tubes, which employ an electrical field to accelerate electrons before decelerating them onto an anode, are based on a similar idea. This must be done in a vacuum to avoid electron collisions with gas particles. The deceleration causes incident x-rays to be generated, which are subsequently directed onto the test specimen (Lu *et al.*, 2021).

A scintillation counter absorbs the x-rays generated by the specimen. The crystal atoms emit light when the x-rays interact with the crystals in the scintillation counter. The amount of energy provided to the crystal by the x-ray quantum determines the intensity of light in this scintillation flash (Lodeiro *et al.* 2009). The flash's light energy strikes a photocathode, which converts it into a voltage pulse. The voltage is proportional to the energy of the emitted radiation by the atom. This energy level is then compared to known x-ray properties to establish which materials are present.

2.9.4 X-ray Diffraction

It’s used to identify crystalline phases qualitatively based on their diffraction pattern. A crystal is formed by atomic/molecular groupings that form a lattice. There are multiple parallel planes known as lattice planes within this lattice, and the distance between these planes is known as the lattice plane distance. Whenever two separate lattice surfaces are struck by parallel x-rays, each atom acts as the scattering center, generating a second wave (Lodeiro *et al*., 2009).

2.9.5 UV-Visible Spectrophotometer

A UV-Visible spectrophotometer (figure 17) measures how much ultraviolet or visible light a substance in solution absorbs, with a more concentrated solution absorbing less (Behera *et al*., 2012).

Figure 17. UV-Visible Spectrophotometer

The UV-VIS spectrophotometer measures absorbance, which may be used to compute a molecule's concentration. It works by light passing from a bulb through a monochromator, which splits it into various wavelengths (see figure 18). A movable slit allows light of a certain wavelength to penetrate into the sample, which is enclosed in a cuvette which is transparent. On the other side of the cuvette, a photoelectric tube monitors the amount of light going through the sample. The amount of transmitted light is measured and converted to absorbance (Behera *et al*., 2012).

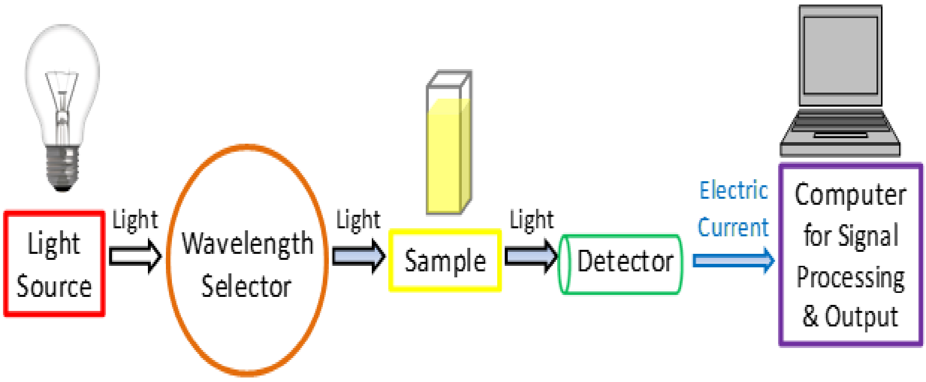


Figure 18. UV-VIS Spectrophotometer working principle

In two methods, a spectrophotometer may be used to determine the concentration of unknown liquids. Method one involves developing a standard curve, a graph of absorbance against concentration for a given standard solution. After that, the absorbances of the unknown solutions are compared to the norm (Behera *et al*., 2012). The Beers-Lambert law, which describes the wavelength at which a substance efficiently absorbs and offers a standard curve indicating a linear relationship between concentration and absorbance, is the second method. The extinguishment coefficient is used to calculate a chemical's concentration under similar instrument conditions (Behera *et al*., 2012). In Equation 6, the Beers-Lambert rule is used to demonstrate the connection between absorbance and concentration.

$A = \varepsilon L c$ .... Equation 6

where, A=absorbance, ε=absorptivity, L=path length c=concentration of solute. Both ε and L are constant so absorbance is directly proportional to the concentration c (Behera *et al*., 2012).

CHAPTER THREE

METHODOLOGY

3.1 Materials

All of the utilized chemicals were of analytical quality and were purchased from Sigma Aldrich. The following chemicals were used: sodium hydroxide pellet (NaOH, 98%), hydrochloric acid (HCl) (35.5%), ammonium hydroxide (NH_4OH, 99.95%), distilled water (H_2O), sulphuric (VI) acid H_2SO_4 (97%), Rhodamine Blue (RB, 95%), glutaraldehyde (GA, 70%), and diclofenac (DCF, 98%).

3.2 Preparation of Adsorbate

Before the studies, stock solutions of RB and DCF were made at 1 gL^{-1} and diluted to the necessary concentrations using the dilution procedure (equation 7).

$$C_1V_1 = C_2V_2 \text{..Equation 7}$$

where C1 is the concentration of the stock solution, V1 is its volume, C2 is the concentration of the diluted solution, and V2 is its volume.

3.3 Preparation of Irish Potato Peels Powder (IPPP)

Irish potato peels were gathered from a hotel at Chuka University, well cleaned with ordinary tap water, and then left to dry in the sun for three days. To remove any dust, dry IPPs were cleaned with distilled water. The cleaned IPPs were pulverized in an electric grinder after being dried at 100oC for 24 hours. Using a sieve with a mesh size of 250 microns, the IPPP was sieved and packed in a sealed plastic container for usage afterwards. Figure 19 depicts the powdered Irish potato peels after sieving. The grinding and washing were carried out at Chemistry Laboratory, Chuka University.

Figure 19. Irish Potatoes Peels Powder after Sieving

3.4 Preparation of Rice Husks Ash (RHA)

Figure 20(a) shows rice husks acquired from Mwea Mills at Mwea Market in Kirinyanga County, Kenya, then washed thoroughly using distilled water for eliminating any sticking contaminants. The washed rice husks were air-dried at ambient temperature before being burned in a furnace at 700^oC for 2 hours to produce ash made from rice husk, as indicated in the figure 20(b). The cleaning and ashing procedure were carried out at Chemistry Laboratory, Chuka University.

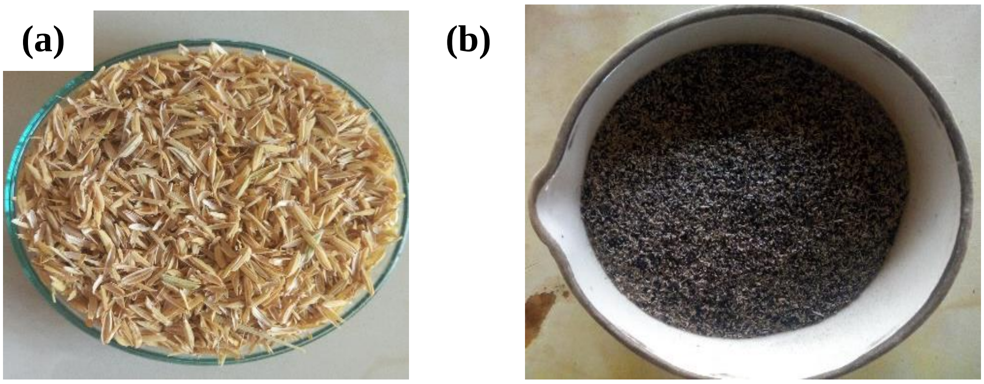


Figure 20. (a) Rice Husk (B)Rice Husk Ash

3.5 Pure Silica Extraction from RHA

Figure 21(a) shows a 30g sample of Rice Husk Ash swirled in 100 ml of 2.5N sodium hydroxide solution and heated for 3 hours in a 250 ml conical flask. Aluminum foil covered the 250 ml conical flask to prevent the contents from entirely evaporating. To completely eliminate the sodium silicate that was present, the residue was rinsed with 30 ml of boiled water after the resultant mixture was filtered, as shown in figure 21(b),

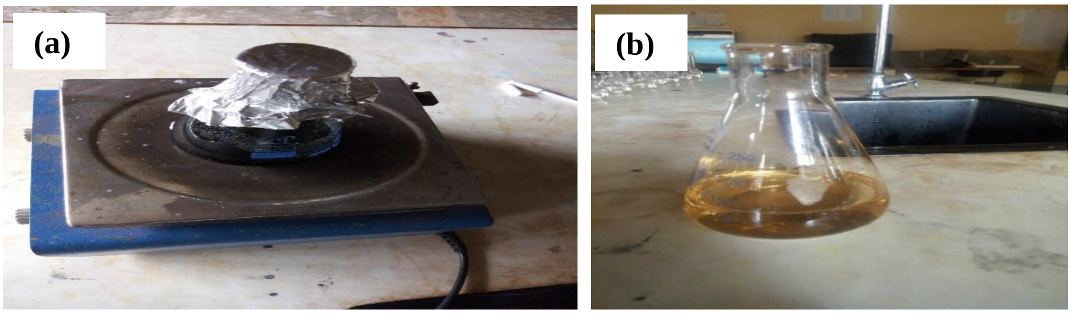


Figure 21. (a) Rice Husk Ash in 2.5M NaOH (b) Sodium Silicate Solution

2.5M H_2SO_4 was added, after allowing the solution to cool to 25^oC until it reached pH 2. After adding 2M NH_4OH pH was adjusted to 8.5, the liquid was allowed to settle to 25^oC. Filtering was done to the resultant solution, and the residue was air-dried in a

150^{o}C oven for 20 hours. Figure 22(a-c) shows precipitated silica following the addition of 2.5M H_2SO_4, silica gel after filtering, and silica after drying. A weighing scale was used to weigh the resultant pure silica. The pure silica was prepared at chemistry laboratory, Chuka University.

Figure 22.(a)Precipitated Silica after Addition of 2.5M H_2SO_4(B) Silica Gel after Filtration(C) Silica after Drying

3.6 Nano Silica Preparation

20g of distilled water many times to eliminate the acid. It was then dissolved in 2M NaOH on a pure silica was heated with 100 ml of 4 M HCl for 4 hours before being rinsed with magnetic stirrer for 2 hours before being adjusted to pH 8 with concentrated H_2SO_4. The silica precipitate was washed with distilled water many times until completely alkaline free filtrate was obtained. The completed product was dried in an oven at 100^{o}C for 24 hours. Figure 23 depicts the drying of nano silica.

Figure 23.Nano Silica after Drying

3.7 Preparation Irish Potatoes Peels Powder- Nano Silica Composite (IPPP–NSC)

In a 250 ml three-necked flask, 10g Silica Nano Particles were dispersed in 100 ml distilled water, then 5g Irish potatoes peels powder added and the mixture agitated. The solution was adjusted to pH 8 with ammonia and agitated for 6 hours at 100°C. The mixture was treated with glutaraldehyde and then agitated for 2 hours at 100°C.

The composite adsorbent geneated (IPPP-NSC) was rinsed and dried with deionized water.

3.8 Characterization of IPPP-NSC

3.8.1 Structural Properties

XRD of powder was carried out on a Bruker D8 Advanced diffractometer (Geology and Mines, Kenya) was used to evaluate the structural properties of the composite. CuK radiation (25 kV and 400 A) was employed to obtain diffraction patterns. XRD samples were coarsely powdered before being put on a glass slide. FTIR spectra were obtained by scanning the material with a Shimadzu IRAffinity-1S FT-IR spectrophotometer (Chuka University) at a wavelength of 4000 to 400 cm^{-1} and 4 cm^{-1} resolution. To prepare materials for FTIR analysis, the KBr pellet technique was utilized. The scrutiny was done in chemistry laboratory Chuka University.

3.8.2 Textural Properties

On a Micromeritics (ASAP 2000) analyzer (University of KwaZulu-Natal), the Brunauer-Emmett-Teller (BET) technique was utilized to get the precise surface area of the composite. The samples were degassed at 383 K for 2 hours before being examined using liquid nitrogen adsorption and desorption at 77 K. The porosities of the samples were measured with the Micromeritics porosity analyzer (ASAP 2000) (University of KwaZulu-Natal) using the Barrett, Joyner, and Halenda (BJH) technique.

3.9 Adsorption Studies

3.9.1 Batch Equilibrium Studies

Batch studies were carried in 250ml clean Erlenmeyer flasks with varied doses of RB and DCF solutions ranging from 1mg/l to 5mg/l and 10mg/l to 40mg/l, respectively. A certain quantity of adsorbent dosage was mixed with RB/DCF solution and shaken at 120rpm. The adsorbent dosage, pH, interaction length, temperatures, and starting concentration were all investigated while other variables remained constant. The solutions were examined using a Ultraviolet-visible spectrophotometer (UV-1800 Shimadzu at Chuka University) after filtration. The percentage of RB dye and DCF removal was determined using Equation 8 below.

$$\% \ removal = \frac{Ci - Ce}{Ci} X\ 100 \ldots\ldots\ldots\ldots\ldots\ldots \text{Equation 8}$$

where Ci is the starting concentration in milligrams per litre and Ce is the equilibrium concentration in milligrams per litre. To obtain adsorption capacity Qe, equation 9 was used.

$$Qe = \frac{Ci - Ce}{M}\ X\ V \ldots\ldots\ldots\ldots\ldots\ldots \text{Equation 9}$$

Where Qe is the adsorbent capacity in mg/g, Ci is the starting dye/DCF concentration in mg/l, M is the adsorbent masses and V is the solution volume.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 FTIR Characterization

4.1.1 Rice Husk Ash FTIR Spectrum

Figure 24 shows the FTIR spectrum of Rice husk ash, which shows characteristic bands of symmetric and asymmetric O-Si-O stretching vibrations at 799.53 cm^{-1} and 1097.54 cm^{-1}, respectively (Farshid *et al*., 2015). The peak at 464.86 cm^{-1} is caused by the vibrations from the bending of O-Si-O. Peaks at 1635.71 cm^{-1} and 3483.59 cm^{-1} represent the stretching and bending vibrations of silanohydroxyl, respectively. (Majid *et al.*, 2014).

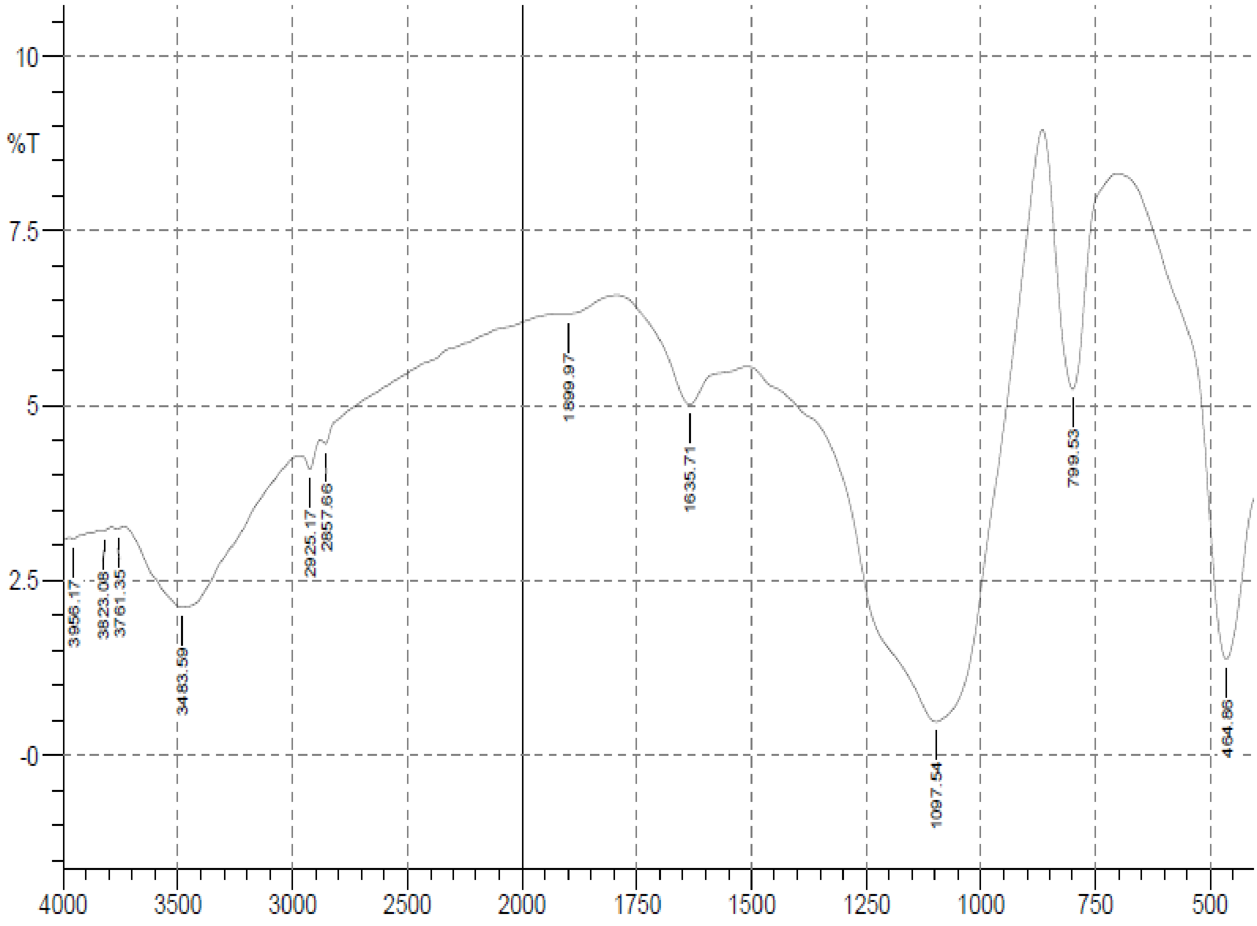


Figure 24. FTIR Spectrum of RHA

4.1.2 FTIR Spectrum of Rice Husk Nanosilica

The spectra in Figure 25 reveals significant peaks at 464.86 cm^{-1}, 620.14 cm^{-1}, and 1107.19 cm^{-1}, showing the existence of nanostructured SiO_2. Bending vibrations of O-Si-O produce the peaks at 464.86 cm^{-1} and 620.14 cm^{-1}. The 800 cm^{-1} band is caused by the symmetric O-Si-O stretching bond vibration, whereas the peak at 1107.19 cm^{-1} is caused by the asymmetric stretching vibration of the O-Si-O bond (Farshid *et al.*, 2015). The signal at 1650 cm^{-1} is attributed by An et al. (2010) to OH bending in the adsorbed water molecule on the nano-silica surface. The stretching frequency of the silanohydroxyl group is given to the broad peak at 3442.12 cm^{-1}. (Majid *et al.*, 2014).

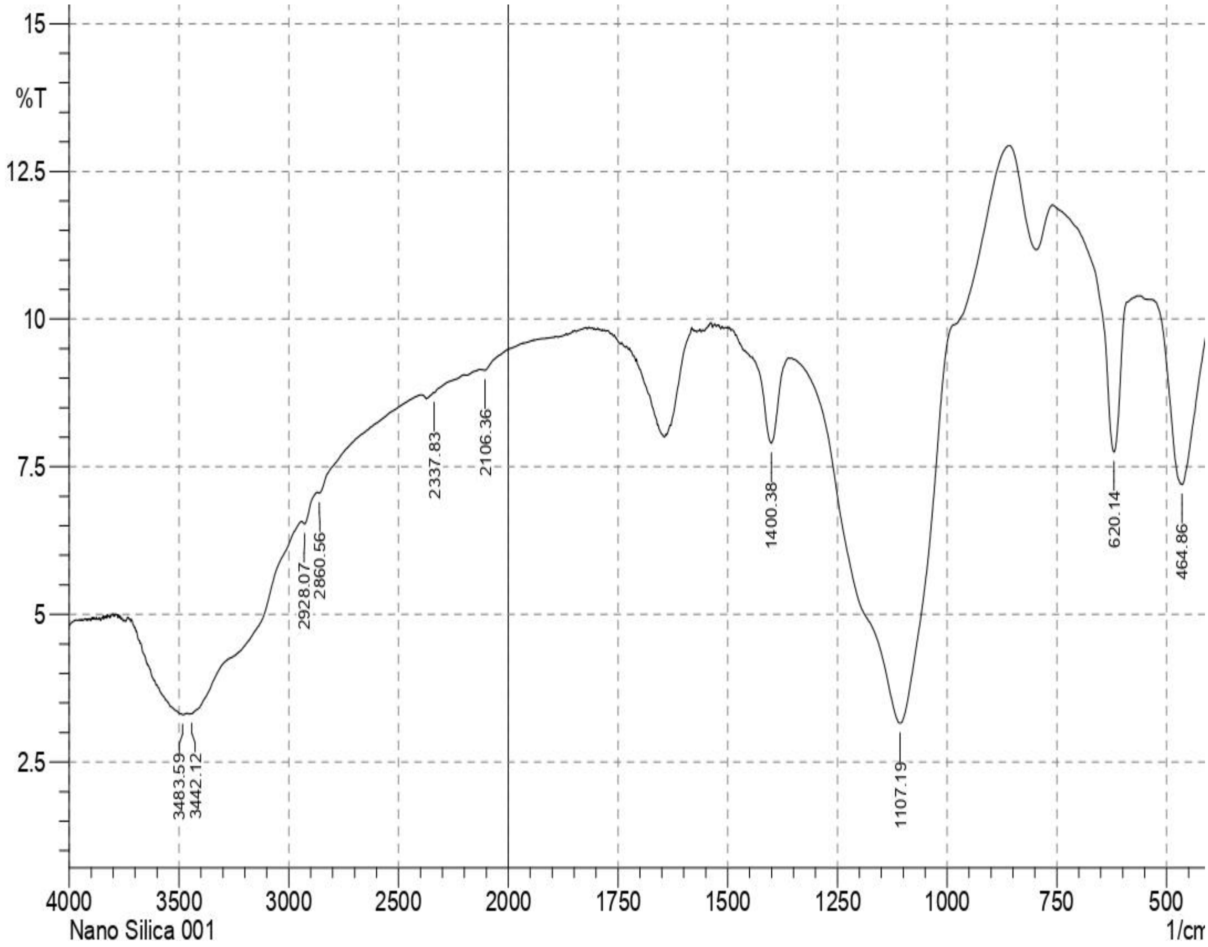


Figure 25. FTIR spectrum of Rice Husk Nanosilica

4.1.3 FTIR Spectrum of Irish Potatoes Peels Powder

Figure 26 depicts an FTIR spectrum with a broad band at 3305.17 cm^{-1}, demonstrating the free H-bonded presence and -OH stretching vibrations of the hydroxyl group in polymers such as cellulose and lignin (Ahmed *et al.*, 2014; Rao *et al.*, 2006). The presence of water molecules on the adsorbent surface causes the broadness. The stretching vibrations of the C = C carbonyl functions correspond to the band at 1645.35 cm^{-1} (Bodirlau *et al.*, 2009; Khairiraihanna *et al.*, 2015). Another peak at 1028.10 cm^{-1} was observed, which is due to C-O-C elongations of the cellulose functionalities seen in potato peels (Bansal *et al.*, 2009). According to the FTIR fingerprint area, hemicellulose is the main component (Yang *et al.*, 2007).

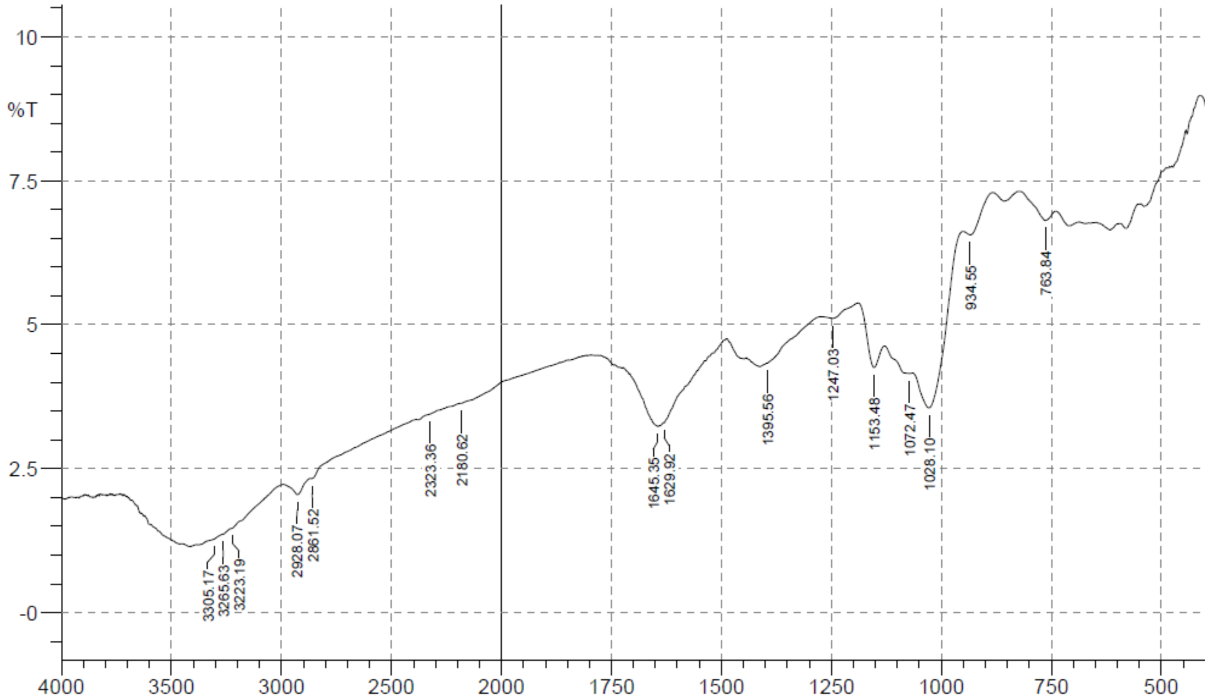


Figure 26. FTIR Spectrum of Irish Potatoes Peels Powder

4.1.4 FTIR Spectrum of IPPP-NSC

Figure 27 shows the composite's spectrum, which shows peaks related to functional groups found in Nano silica and Irish potatoes peels powder, indicating that the composite was effectively constructed. Absorption peaks at 467.76cm^{-1}, 606.64cm^{-1}, and 1104.29cm^{-1} suggest the existence of nanostructured SiO_2 (Farshid *et al.*, 2015). The peaks at 467.76cm^{-1} and 606.64cm^{-1} are caused by O-Si-O bending vibrations. Asymmetric O-Si-O stretching is responsible for the peak at 1104.29 cm^{-1} (An *et al.*, 2010). The 3439.23 cm^{-1} broad peak is assigned the stretching frequency of the silano hydroxyl group (Farooq *et al.*, 2011). The peak at 1645.35 cm^{-1} represents OH bending vibration in water molecule (Bansal et al., 2009) which illustrated clearly the potato peel powder blended well with the Nano silica hence the presence of both functional groups of silica and potatoes peels powder in the spectrum.

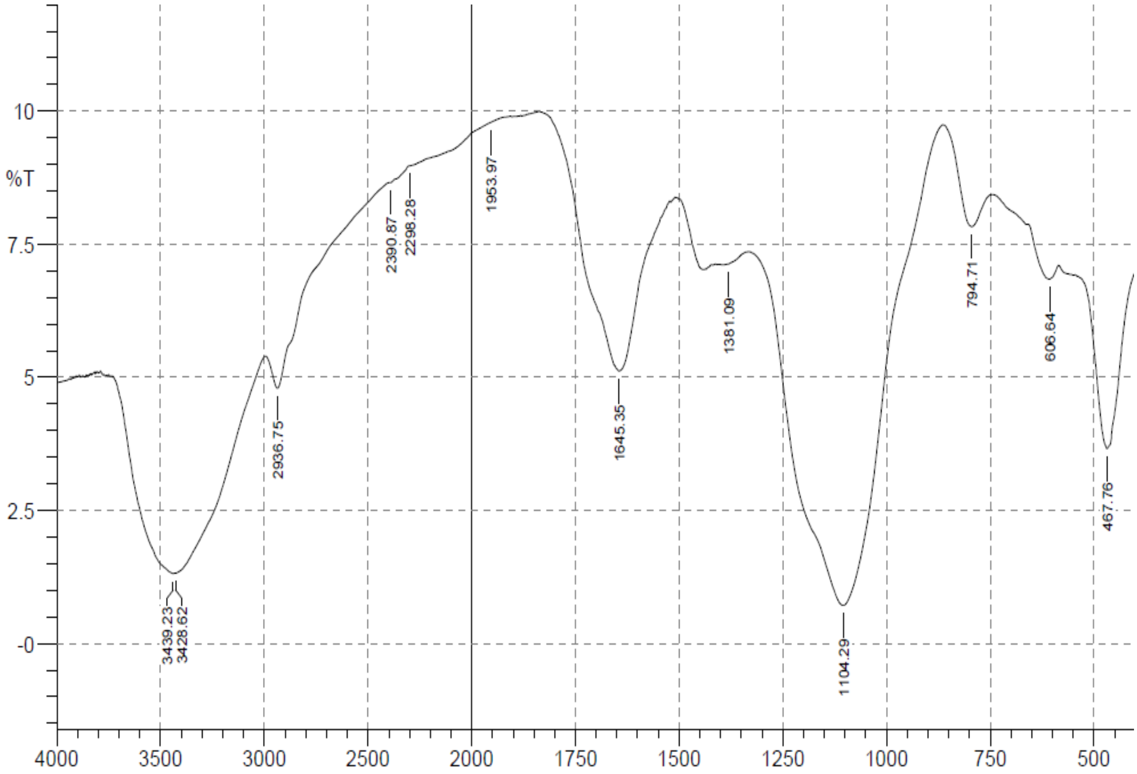


Figure 27. FTIR Spectrum of IPPP-NSC

4.2 XRD Analysis of Composite

XRD diffractograms of composite in Figure 28(c) showed strong broad peak between 20^o and 25^o (2θ) that suggested characteristic of amorphous SiO_2 in the composite. The XRD pattern of the composite has not changed significantly since both Irish potato peels powder figure 28(a) and rice husk nano silica figure 28(b) synthesized are amorphous in nature (Ramezanianpour *et al*., 2009).

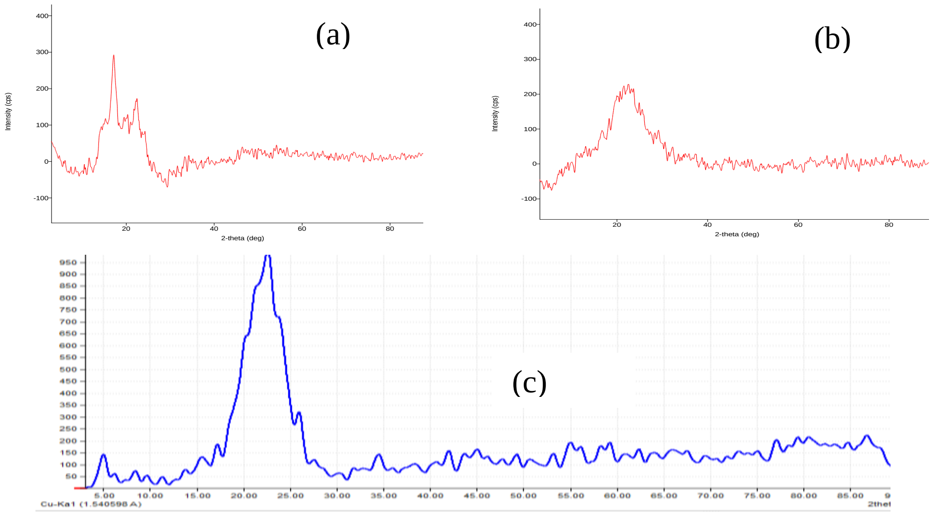


Figure 28. (a)XRD Diffractograms of Potatoes Peels Powder (b) Nano silica (c) IPPP-NSC Composite

4.3 BET Adsorption

The surface area calculated by BET was 100.6328 m^2/g with a single point surface area of 97.4036m^2/g at P/Po=0.300844548 and average pore diameter of 179.345 Å. when a composite adsorbent has larger surface are, it is very efficient in adsorption of contaminants (Wang *et al.*, 2022). Figure 29 depicts the composite adsorbent's nitrogen adsorption-desorption isotherm curve. The findings showed that the N2 isotherm behavior conformed to the IUPAC (International union of pure and applied chemistry) organization's type III adsorption/desorption isotherm.

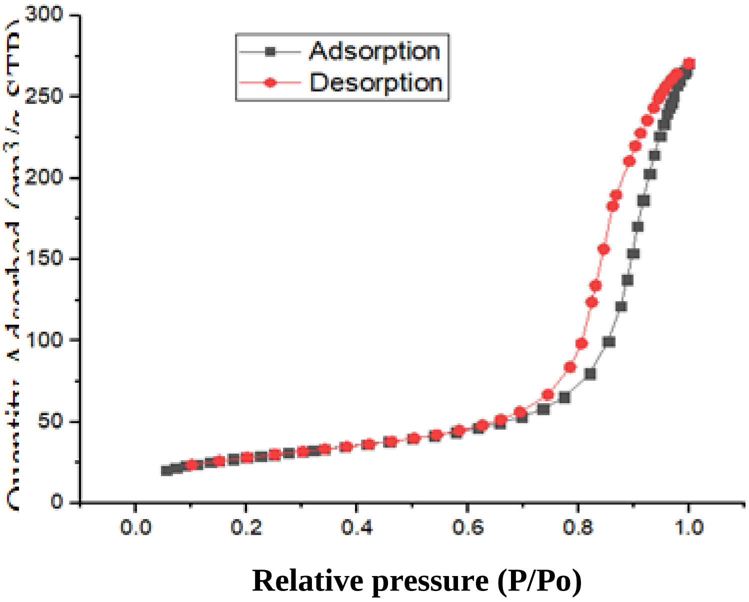


Figure 29. BET-BJH of the Composite

4.4 Elemental Analysis

Table 1 shows the composition of main elements in the composite as determined by the X-ray fluorescence (XRF) technology. Percentage of SiO_2 was 97.95% and that of MgO was 1.146%. All other elements were below 1%. The results show silica formed larger percentage of the composite is confirming the ratio of mixing the two adsorbents, IPPP and RHNS

Table 1:
XRF Analysis of the Composite

Element	MgO	SiO_2	P_2O_5	S	Cl	K_2O	Ti	Mn	Fe
% Composition	1.146	97.95	0.09	0.61	0.004	0.045	0.020	0.011	0.08

4.5 Adsorption Studies

4.5.1 Effect of IPPP-NSC Mass Ratio

The adsorption of RB and DCF by different composite adsorbents with different mass ratios of IPPP and RHNS is shown in figure 30. The removal percentage of RB and DCF is higher in the composite synthesized than in IPPP and RHNS. Further there is increase in removal percentage of RB and DCF as the content of silica increases until the ratio is 4:1(4g of RHNS/1g of IPPP). Increasing RHNS to 5g results in decrease in adsorption capacity. Therefore, the best composite ratio used in this study was 4:1 for RHNS to IPPP.

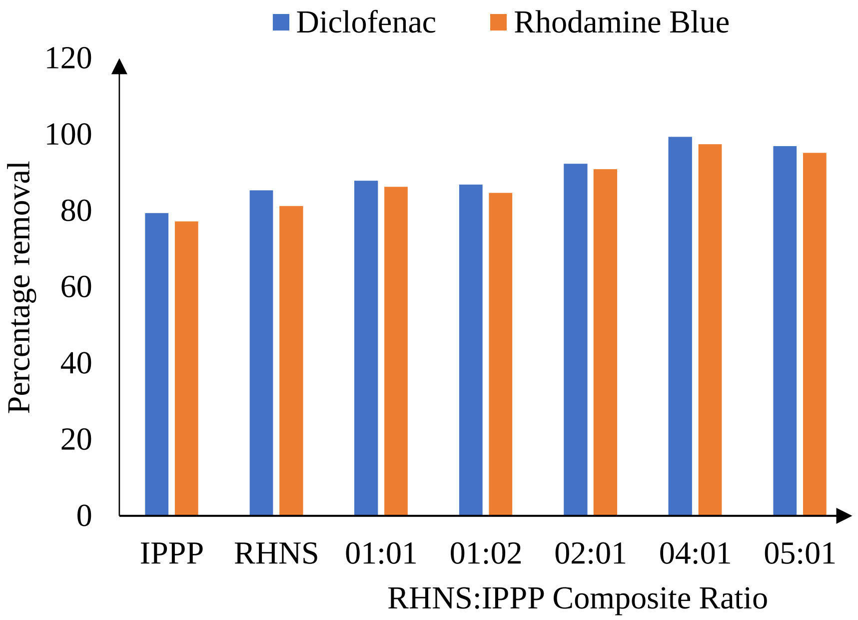


Figure 30. Effect of IPPP-NSC Mass Ratio on DCF and RB Adsorptions

4.5.2 Adsorption Studies of Rhodamine Blue

4.5.2.1 The Effect of pH on RB Removal

The influence of solution pH on Rhodamine Blue sorption was investigated using 0.1 g of IPPP-NSC, 1mg l^{-1} dye initial concentration, pH range of 2 to 10 at 25 °C, contact time 80min and shaking speed of 120rpm. Figure 31 shows the results of adjusting the pH using 0.05 M hydrochloric acid and 0.05M sodium hydroxide. In the pH level ranging from 2 to 4, there was an increase in efficiency of removal for RB from 86.8 to 97.4%, whereas at pH level of 4 to 8 made the adsorption capacity of IPPP-NSC to RB relatively stable. Moreover, as seen in figure 31, there were significant decreases in RB removal effectiveness as pH increased from 8 to 10. This result was attributed to the change in molecular form of RB at high pH values. Dye molecules becomes difficult to disperse into the adsorbent surface pores, resulting in a reduction in adsorption efficiency (Patra *et al*., 2022).

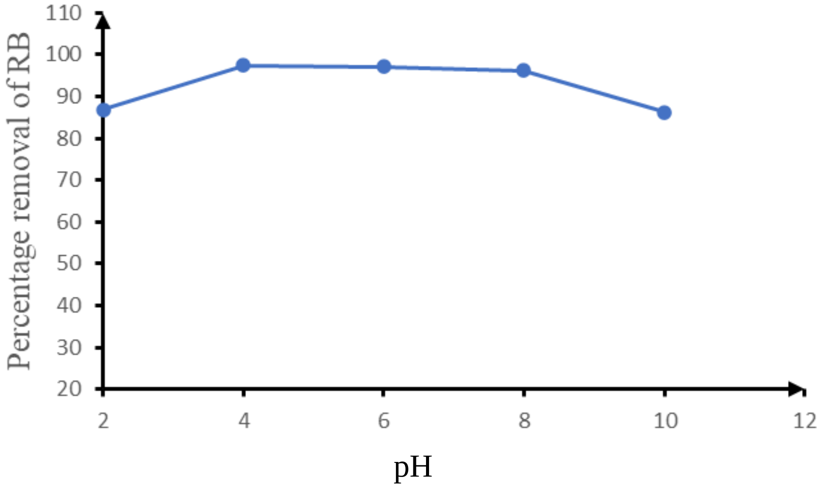


Figure 31. Effect of pH on Removal of RB

4.5.2.2 Effect of Contact Time on Removal of RB

The influence of contact time on RB sorption was evaluated for an 1mgl^{-1}initial dye concentration, an adsorbent mass of 0.1 g, a solution volume of 20 ml, a shaking speed of 120 rpm, and 25^{0}C temperature. The dye absorption increased over time until it reached a constant value where no additional dye was absorbed from the solution, as seen in figure 32. At this point, the amount of adsorbed dye onto the adsorbent was in dynamic equilibrium with the amount of sorbent. dye desorbed.

The amount of dye adsorbed at the equilibrium time revealed the sorbent's maximum dye adsorption capacity under these precise circumstances (Errais *et al*., 2011). The needed contact time to reach balance is 80 minutes. The rapid sorption seen during the first 80 minutes is due to the active sites availability on the IPPP-NSC surface; however, when these active sites are gradually occupied, the sorption becomes less effective (Errais *et al*., 2011).

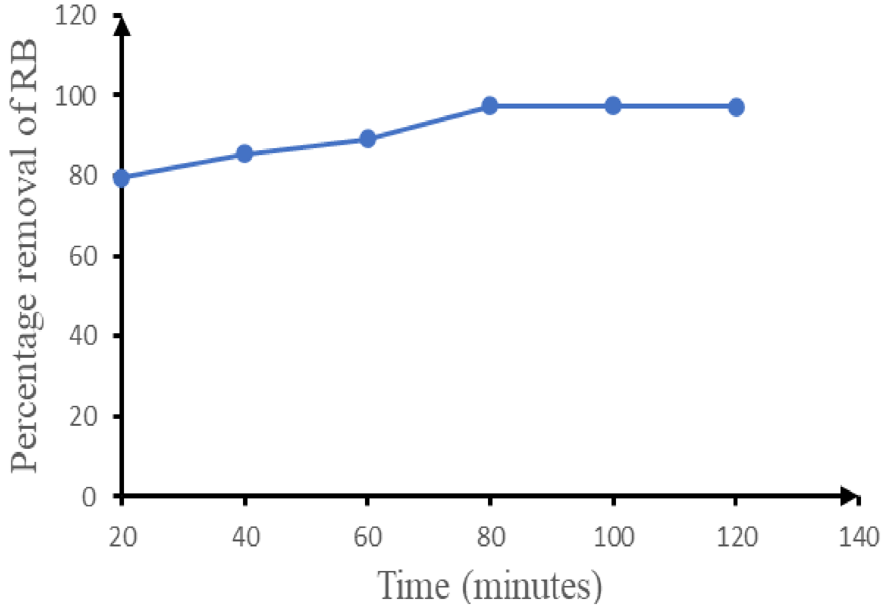


Figure 32. Effect of Contact Time on Removal of RB

4.5.2.3 Effect of Adsorbent Dosage on Removal of RB

An experiment was set up to investigate the effects of applied IPPP-NSC doses on Rhodamine blue adsorption. The dosages ranged from 0.1 to 0.5 mg/20 mL, with a solution pH of 4, an initial concentration of 1 mg/L, an 80-minute contact duration, and a whirling speed of 120 rpm. The dye absorption data utilizing various doses of IPPP-NSC are depicted in Figure 33. The (qe) equilibrium dye uptake capacity was shown to decrease with increasing adsorbent dose, with 0.1 g being the best.

The splitting effect of the concentration gradient between the adsorbate and adsorbent reduced the dye absorption value. It is explained by the interaction of adsorbent molecules, which results in the adsorption of RB molecules from the adsorbent's narrow sites, and the reduction of particular surfaces, which results in the creation of an adsorbent particle aggregation (Pourjavadi *et al*., 2016). These decreases might potentially be the result of adsorption site unsaturation. According to these observations, as the dose of each adsorbent increases, so does the number of adsorbent sites available to the dye molecules, resulting in ineffective adsorption. Another result is a decrease in active sites at the surfaces of the absorbents, as well as a decrease in dye matter rate transfer at the surfaces of the absorbents, implying that the dye quantity adsorbed per unit mass of adsorbent is restricted by the adsorbent dose (Ma *et al.*, 2012).

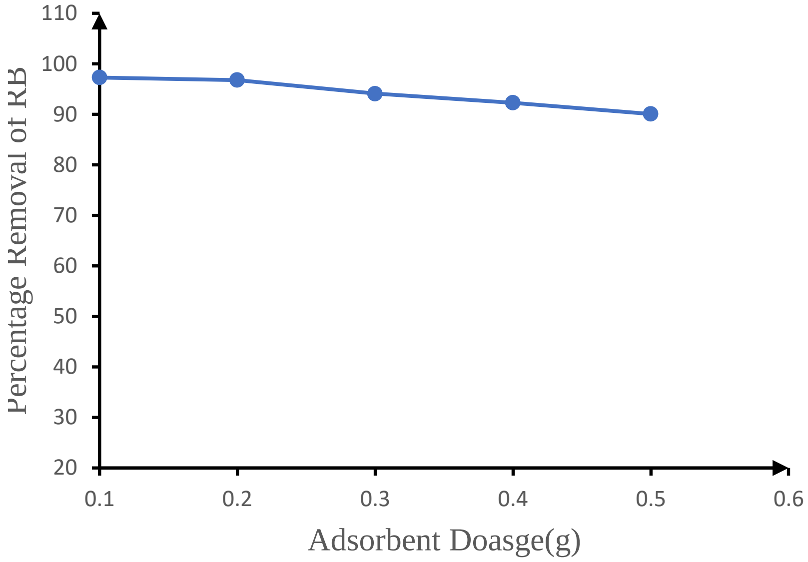


Figure 33. Effect of Adsorbent Dosage on Removal of RB

4.5.2.4 Effect of Temperature on Removal of RB

Adsorption studies were carried out at three distinct temperatures: 25 35, 45, and 55 °C, with an initial RB concentration of 1 mg/L, a solution pH of 4, a swirling speed of 120 rpm, and a contact period of 80 minutes. The results reveal that raising the temperature from 250 C to 550 C lowered the removal efficiency of RB from 97.47% to 91.26% (figure 34). This is due to the fact that the adsorption process is exothermic (Boumchita *et al.*, 2016).

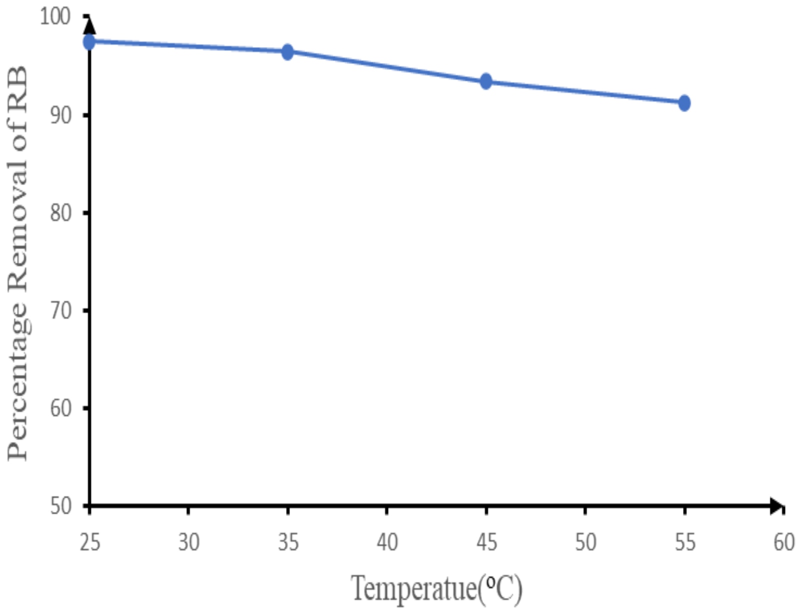


Figure 34. Effect of Temperature on Removal of RB

4.5.2.5 Effect of Initial Dye Concentration on Removal of RB

Figure 35 results show that as the initial amount of dye increases, so does the fraction of dye remove. Because more dye particles in solution, occupy accessible binding sites on adsorbent at lower concentrations, adsorption is improved. However, at larger concentrations, the adsorbent's accessible sites become constrained, and no further adsorption occurs (Sulyman *et al.*, 2020). Increasing initial adsorption capacity increases with dye concentration because the interaction between the dye and the adsorbent improves. (Goswami and Phukan, 2017).

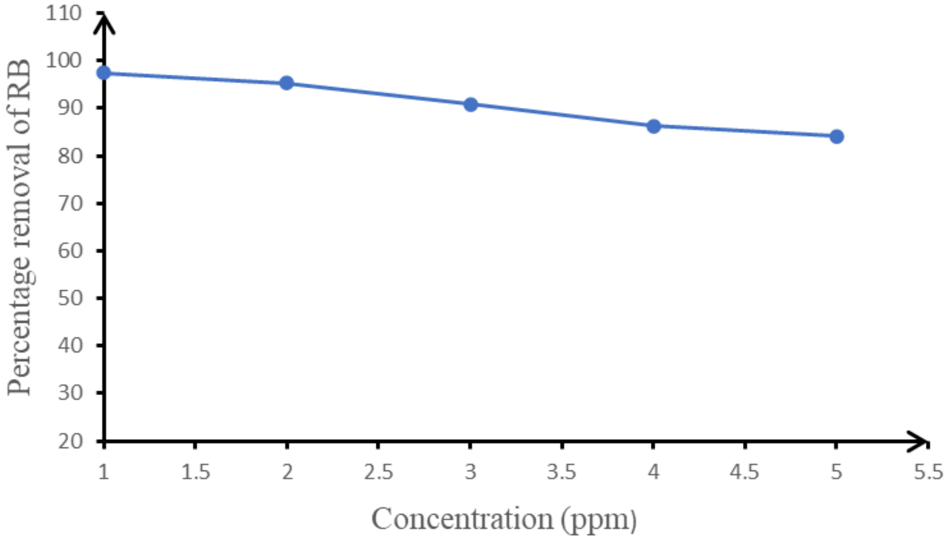


Figure 35. Effect of Initial Dye Concentration on Removal of RB

4.5.3 Adsorption Studies of DCF

4.5.3.1 Effect of Contact Time on Removal of DCF

Figure 36 depicts the contact time effect on the percentage of diclofenac sodium elimination. DCF adsorption on IPPP-NSC increases with contact time, and DCF adsorption reached equilibrium after 60 minutes. The adsorption capacity of DCF rose dramatically within the first 60 minutes.

This quick adsorption ability of IPPP-NSC demonstrated a larger driving force in the first stage, resulting in the rapid transfer of DCF to the surface of IPPP-NSC particles (Lu *et al*., 2016).

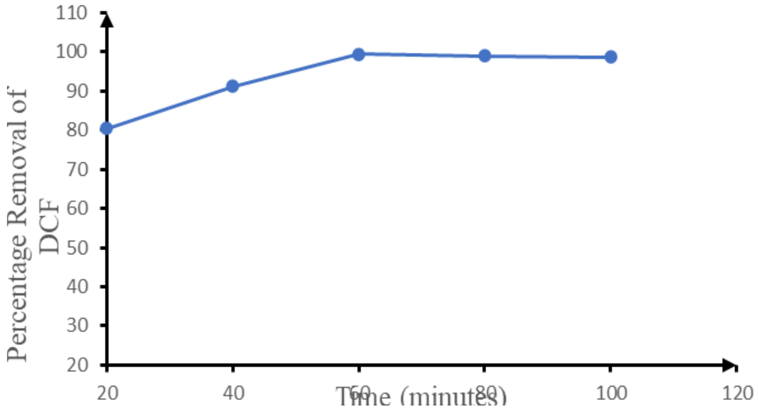


Figure 36. Effect of Contact Time on Removal of DCF

4.5.3.2 Effect of Adsorbent Dosage on Removal of DCF

The impact of IPPP-NSC dose on removal of diclofenac sodium was studied using adsorbent dosages ranging from 0.025 to 0.1g and a 60-minute adsorption period to achieve equilibrium. As shown in figure 37, increasing the adsorbent dose from 0.025g to 0.1g increased the percentage of DCF removal from 87.41% to 99.5%. This is because more adsorption sites are available, increasing the degree of DCF removal (Jodeh *et al*., 2016).

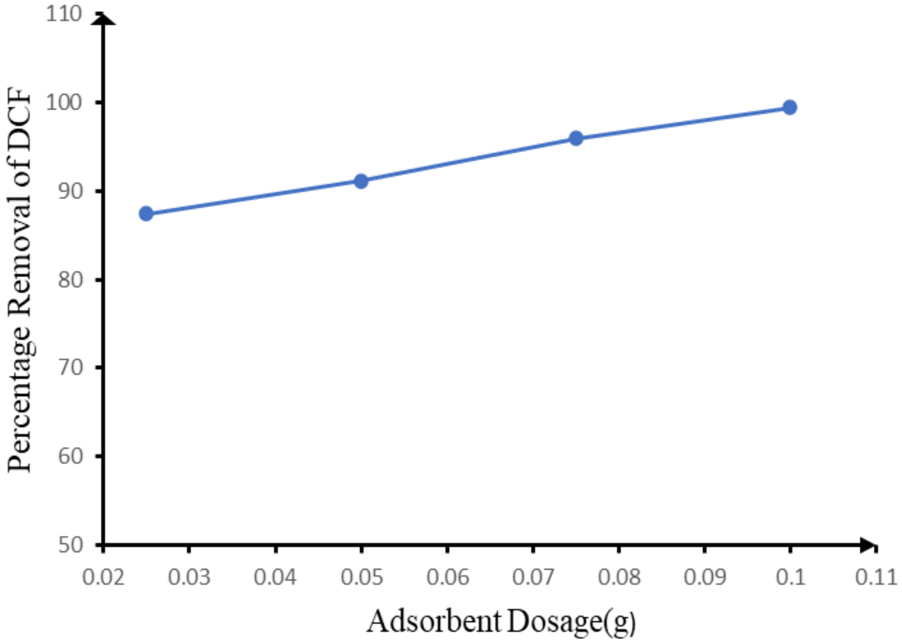


Figure 37. Effect of Adsorbent Dosage on Removal of DCF

4.5.3.3 Effect of pH on Removal of DCF

The change of adsorption onto IPPP-NSC was studied in the pH range 2-10. To adjust the pH, sodium hydroxide (0.05M) and hydrochloric acid (0.05M) are utilized. The pH influence on diclofenac sodium elimination was studied using 0.1g of IPPP-NSC and a 60-minute adsorption duration to achieve equilibrium. The optimal pH for diclofenac sodium adsorption, as shown in Figure 38, was 2. When the pH of the solution falls owing to the physical adsorption process, the 'van der Waal' contact between DCF and the composite surface increases (Zhao *et al.*, 2019).

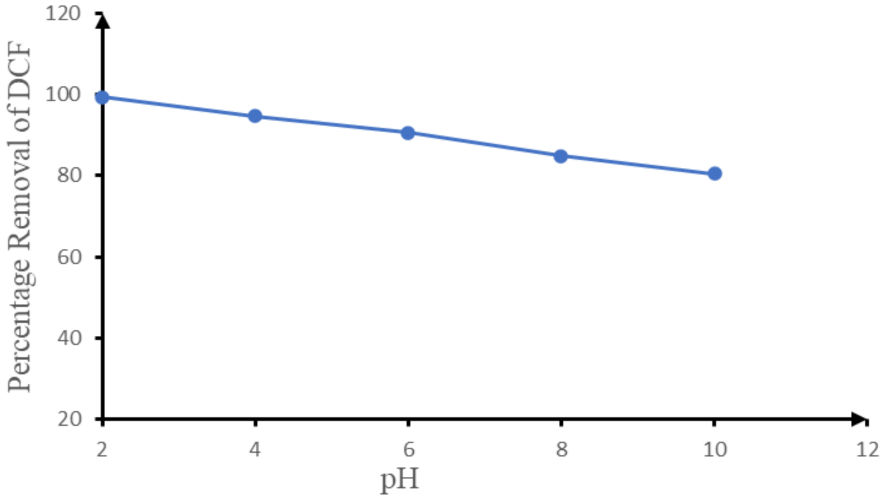


Figure 38. Effect of Ph on Removal of DCF

4.5.3.4 The Effect of Temperature on DCF Removal

Temperature effects on adsorption onto IPPP-NSC were investigated between 25 and 55degrees Celsius. Figure 39 shows how adsorption of diclofenac sodium decreased with increasing temperature. The greatest percentage of adsorption performance of IPPP-NSC at 25°C was 99.36%. Temperature increases DCF solubility in water, which reduces the adsorption process and the attraction forces between DCF and IPPP-NSC (Jodeh *et al*., 2016).

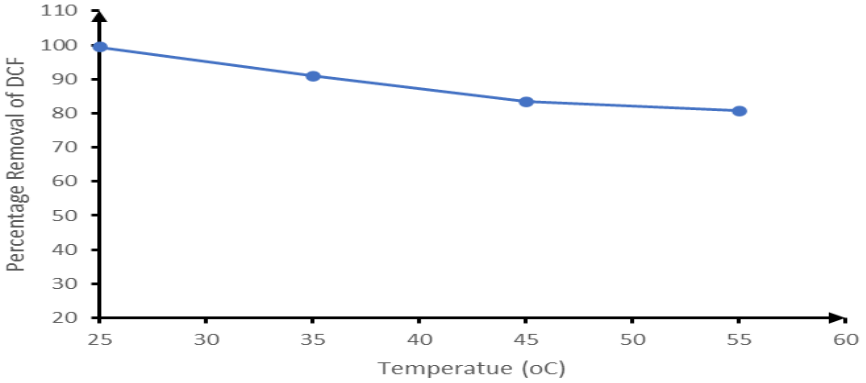


Figure 39. Effect of Temperature on Removal of DCF

4.5.3.5 Effect of Concentration of Diclofenac (DCF)

The impact of diclofenac initial concentration on the percentage removal at equilibrium is shown in Figure 40. As concentration rises, IPPP-NSC removes a greater percentage of DCF. The percentage of removal by PPP-NSC rose from 74.23% to 99.38% when concentration increased from 10mg/L to 40mg/L. When extracting DCF from an aqueous solution using activated carbon made from cyclamen persicum tubers, (Shehdeh *et al.*, 2012) obtained results that were similar.

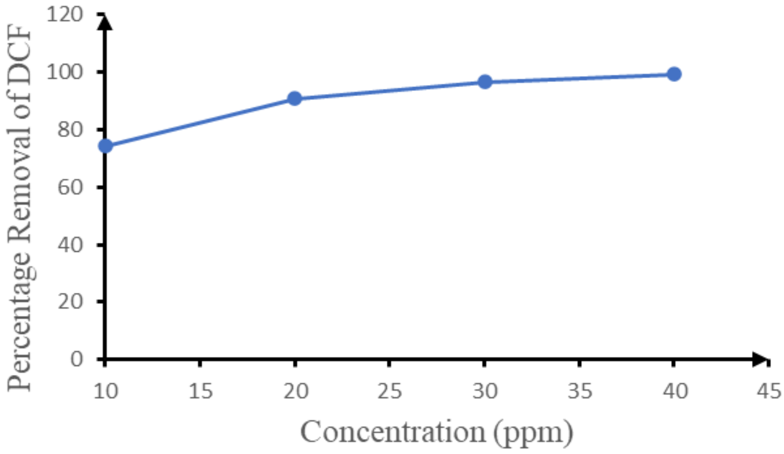


Figure 40. Effect of Diclofenac Sodium Concentration on Removal of DCF

4.6 Adsorption Isotherms

Isotherm equations' appropriateness for forecasting adsorption patterns is crucial for application and industrial design. The degradation equilibrium adsorption data for the RB and DCF by IPPP-NSC were analyzed using the Langmuir and Freundlich models. Figure 41(a & b) shows a linearized Langmuir equation plot for RB and DCF, whereas Figure 42(a & b) shows the Freundlich equation. The regression coefficients for the Langmuir and Freundlich equations are shown in Table 2.

The DCF equilibrium data has a higher correlation coefficient R^2=0.90144 to the Langmuir isotherm equations than the Freundlich R^2=0.86408. This suggests that the IPPP-NSC adsorption sites and energy were spread equally. The Freundlich isotherm, on the other hand, suited the degradation of RB better, with R^2=0.99617 compared to R^2=0.98752 for the Langmuir values. This indicates that the adsorption process happened on a heterogeneous surface where the adsorbent's absorption capability occurred, rather than on a homogeneous site. The observed adsorption pattern corresponded to that obtained by (Inyinbor *et al.*, 2016), who discovered that RB degradation followed the Freundlich isotherm model.

Table 2:
Langmuir and Freundlich Constants

	Langmuir			Freundlich		
Sample	Q_{max} (mg/g)	K_L (Lmg$^{-1)}$	R^2	1/n	K_F (mg/g)	R^2
RB	0.9371	6.972	0.98752	0.40812	0.60981	0.99617
DCF	7.257	1.8954	0.90144	0.60981	20.322	0.86408

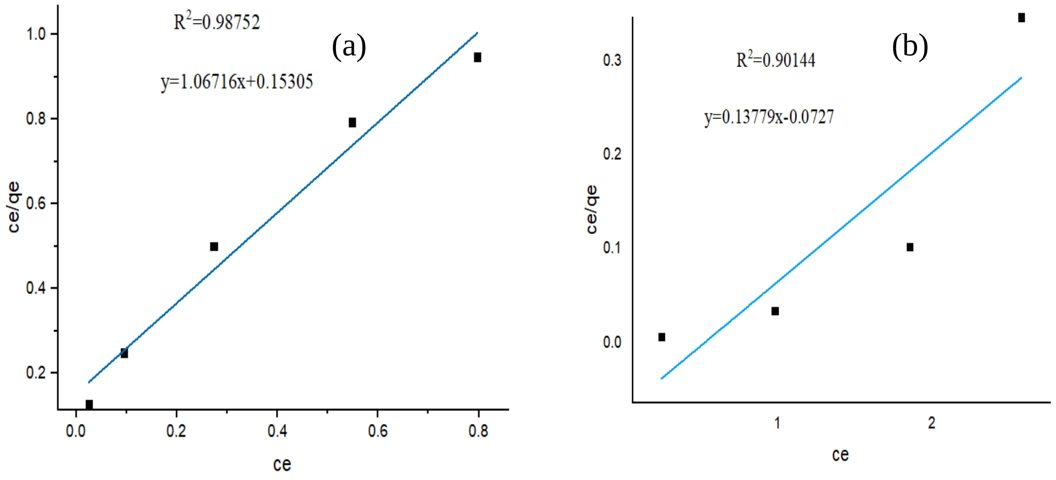


Figure 41. Langmuir Isotherm of RB (a) and DCF (b)

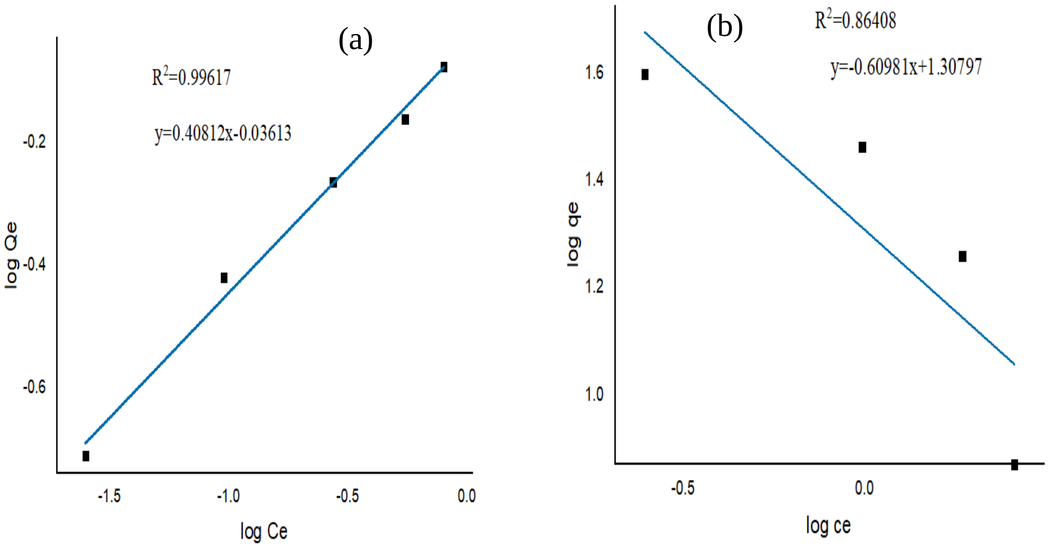


Figure 42. Freundlich Isotherm of RB (a) and DCF (b)

The findings of a research into the factors of the two kinetic models are shown in Table 3. The plots of t/qt against t are shown in Figures 43(a & b) and (qe-qt) against t, in Figures 44(a & b) ln the pseudo second order model characterized the kinetics of RB and DCF adsorption by the composite in terms of correlation of determination close to one, implying that the pseudo second order model can better explain the kinetics of RB and DCF adsorption. The results show that increasing the initial adsorbate concentration raises the initial adsorption rate (mins), implying that mass transfer influences RB adsorption and DCF breakdown (Fu *et al.*, 2015).

As a consequence, the dye molecule was swiftly absorbed by reaching the adsorbent's surface. This might be due to the active sites and functional groups on the adsorbent's surface. According to the pseudo second order model, the removal of RB& DCF was a rate-governing mechanism because a chemisorptive connection was created between the adsorbent and the adsorbate as a result of the composite's absorption ability (shan *et al.*, 2015).

Table 3:
Adsorption Kinetics of RB and DCF

	Pseudo first order kinetic model			Pseudo second order kinetic model		
Sample	K_1 (1/min)	Qe	R^2	K_2(g/mg.min)	qe	R^2
RB	0.1153	0.1301	0.67458	64.387	0.20774	0.9989
DCF	0.0101	7.2297	0.32572	1.5051×10^{-7}	14656.309	0.84946

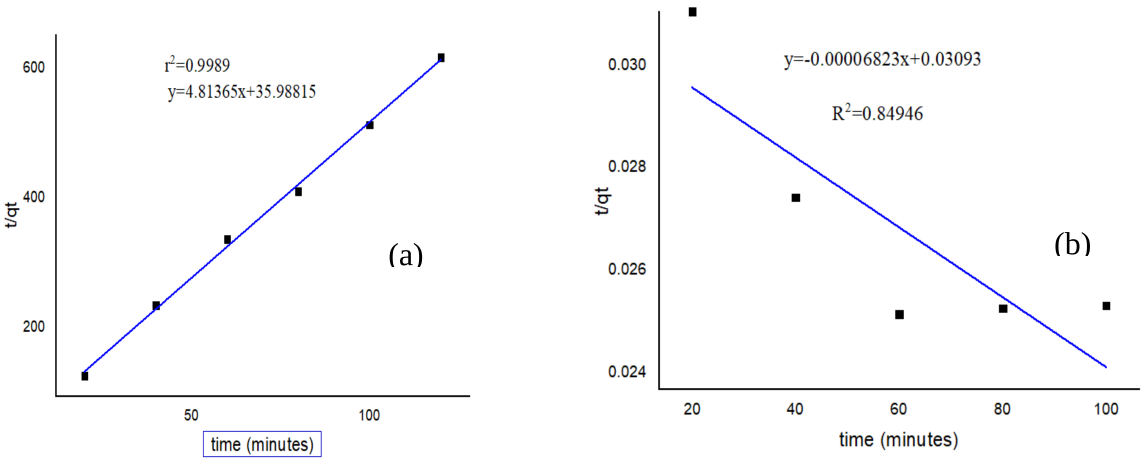


Figure 43. Pseudo Second Order Kinetic of RB (a) and DCF (b)

Figures 44(a & b) shows pseudo first order model characterized the kinetics of RB and DCF.

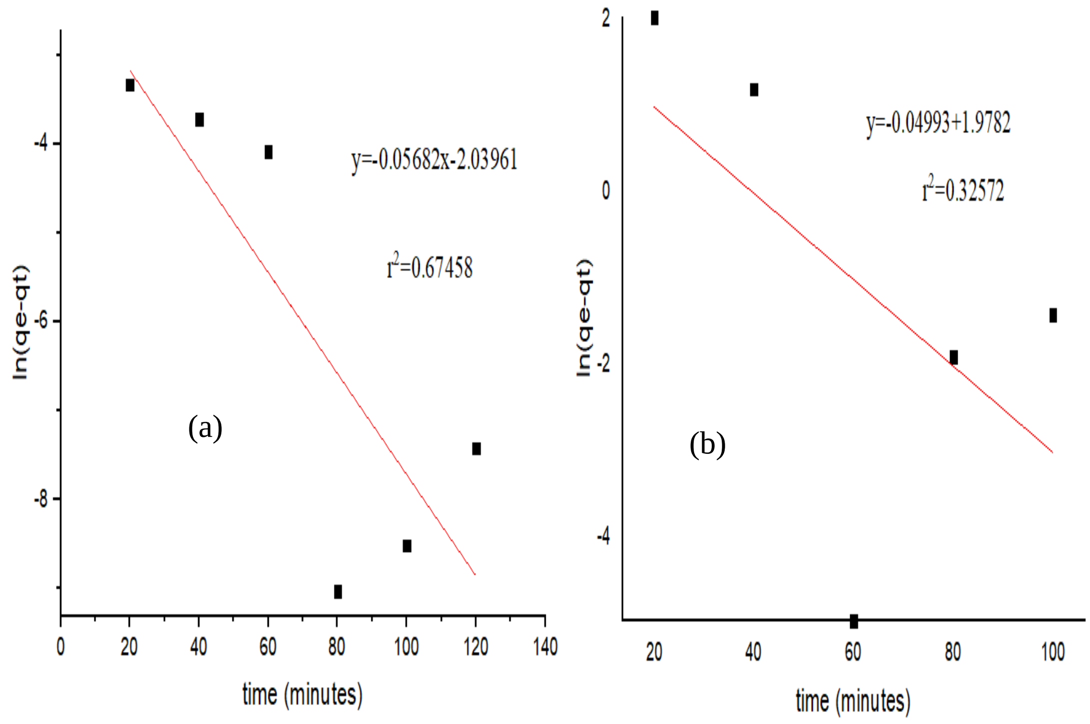


Figure 44. Pseudo First Order Kinetic of RB (a) and DCF (b)

CHAPTER FIVE

SUMMARY, CONCLUSION AND RECOMMENDATIONS

5.1 Summary of Key Findings

The use of IPPP and RHNS to synthesize a composite IPPP-NSC was ascertained. The synthesized composite was subjected to a variety of characterization tests. Fourier transform infrared spectra of the IPPP and Nano silica show that they contain functional groups on their surface. When they are combined to form composite the number of active groups on the solid support surface increases for instance, -OH, C-H, C=C, C-O, C=O, Si-OH, O-Si-O, which are responsible for adsorption of Rhodamine blue and Diclofenac as evidenced in the FTIR spectrum. XRF analysis of the composite revealed silica formed larger percentage in the composite ascertaining the ratio in which RHNS and IPPP were mixed (4:1).

The composite has a surface area of 100.6328m^2/g, with a single point surface area of 97.4036m^2/g at P/Po=0.300844548, according to BJH surface analysis. The average pore diameter was determined to be 179.345 Å. The particle diffraction pattern revealed a diffuse pattern, indicating an amorphous phase, which was verified by XRD patterns.

5.2 Conclusion

The composite's adsorption capability for Rhodamine blue and Diclofenac was optimum at pH 4 and 2, respectively, adsorbent dosage of 0.1g, initial concentrations of 1mg/L and 40mg/L respectively, and agitation speed of 240 rpm. At the optimal temperature of 298 K, the equilibrium between the adsorbate in solution and the adsorbent surface was reached in around 80 minutes for Rhodamine blue and 60 minutes for Diclofenac. The adsorbents' efficiency in removing Rhodamine blue and Diclofenac rises with adsorbent dose up to 0.1 g. At optimum conditions, the removal efficiency of RB was 97.57% while that of DCF was 99.39%.

With an adsorption capacity of 1.0868 mg/g in the composite adsorbent used, the Freundlich isotherm model fit the RB removal best, while the Langmuir isotherm model matched the DCF removal best, with an adsorption capacity of 7.257 mg/g. higher surface area, fineness, and concentration of vacant sites in activated materials are related with higher adsorption capacity.

5.3 Recommendation of the Study

1. Industries should be apprised on the employment of rice husk nanosilica and Irish potato peels powder in treatment of water effluent. Materials are readily available locally.
2. Rice husk nanosilica and Irish potato peels powder be combined to improve efficacy of the adsorbents in removing hues and pharmaceuticals from water.
3. People should be advised on the use of locally accessible agricultural wastes in water purification at home.

5.4 Recommendations for Further Studies

1. In order to make the procedure more cost-effective, studies on synthetic composites should be conducted to see if they may be recycled
2. Studies of IPPP-NSC composite synthesized on the effect of the adsorbents heavy metals should be carried out.
3. More research on the mechanics of adsorption using SEM and EDS should be done to understand how adsorption occurs.

REFERENCES

Abin-Bazaine, A., Trujillo, A. C., & Olmos-Marquez, M. (2022). Adsorption Isotherms: Enlightenment of the Phenomenon of Adsorption. In *Wastewater Treatment*. Intech Open.

Acharya, J., Kumar, U., & Rafi, P. M. (2018). Removal of heavy metal ions from wastewater by chemically modified agricultural waste material as potential adsorbent-a review. *International Journal of Current Engineering and Technology*, *8*(3), 526-530.

Ahmed, M. J. K., Ahmaruzzaman, M., & Reza, R. A. (2014). Lignocellulosic-derived modified agricultural waste: Development, characterization and implementation in sequestering pyridine from aqueous solutions. *Journal of colloid and interface science*, *428*, 222-234.

Ai L, Jiang J (2010). Fast removal of organic dyes from aqueous solutions by AC/ferrospinel composite. *Desalination*, 262: 134-140.

Albrecht, M. A., Evans, C. W., & Raston, C. L. (2006). Green chemistry and the health implications of nanoparticles. *Green chemistry*, 8(5), 417-432.

Ali, H., Ahmad, W., & Haq, T. (2009). Decolorization and degradation of malachite green by Aspergillus flavus and Alternaria solani. *African Journal of Biotechnology*, 8(8), 1574-1576.

Al-Wasidi, A. S., AlZahrani, I. I., Naglah, A. M., El-Desouky, M. G., Khalil, M. A., El-Bindary, A. A., & El-Bindary, M. A. (2021). Effective Removal of Methylene Blue from Aqueous Solution Using Metal-Organic Framework; Modelling Analysis, Statistical Physics Treatment and DFT Calculations. *Chemistry Select*, *6*(41), 11431-11447.

Amaresh, N., Mullaicharam, A. R., & El-Khider, M. A. (2011). Chemistry and pharmacology of caffeine in different types of tea leaves. *International Journal of Nutrition, Pharmacology, Neurological Diseases*, *1*(2), 110.

An, D., Guo Y., Zhu, Y., and Zichen, W. (2010). A Green Route to Preparation of Silica Powders with Rice Husk Ash and Waste gas. *Chemical Engineering Journal*, 162(2): 509-514.

Anastopoulos, I., & Kyzas, G. Z. (2014). Agricultural peels for dye adsorption: a review of recent literature. *Journal of Molecular Liquids*, 200, 381-389.

Baena-Nogueras, R. M., González-Mazo, E., & Lara-Martín, P. A. (2017). Degradation kinetics of pharmaceuticals and personal care products in surface waters: photolysis vs biodegradation. *Science of the total environment*, *590*, 643-654.

Bailey, I. (2017). *New environmental policy instruments in the European Union: politics, economics, and the implementation of the packaging waste directive*. Taylor & Francis.

Bansal, M., Garg, U., Singh, D., & Garg, V. K. (2009). Removal of Cr (VI) from aqueous solutions using pre-consumer processing agricultural waste: A case study of rice husk. *Journal of hazardous materials*, *162*(1), 312-320.

Behera, S., Ghanty, S., Ahmad, F., Santra, S., & Banerjee, S. (2012). UV-visible spectrophotometric method development and validation of assay of paracetamol tablet formulation. *J Anal Bioanal Techniques, 3*(6), 151-7.

Bensalah, H. (2020). *Natural and Synthetic Apatites as Adsorbents for the Removal of Azo Dyes from Aqueous Solutions* (Doctoral dissertation, Technische Universität Berlin).

Benson, A. M., Hunkeler, M. J., & Talalay, P. (1980). Increase of NAD (P) H: quinone reductase by dietary antioxidants: possible role in protection against carcinogenesis and toxicity. *Proceedings of the National Academy of Sciences*, 77(9), 5216-5220.

Bhatnagar, A., & Sillanpää, M. (2010). Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment—a review. *Chemical engineering journal*, *157*(2-3), 277-296.

Bodirlau, R., Teaca, C. A., & Spiridon, I. (2009). Preparation and characterization of composites comprising modified hardwood and wood polymers/poly (vinyl chloride). *BioResources*, *4*(4), 1285-1304.

Carneiro, P. A., Umbuzeiro, G. A., Oliveira, D. P., & Zanoni, M. V. B. (2010). Assessment of water contamination caused by a mutagenic textile effluent/dyehouse effluent bearing disperse dyes. *Journal of hazardous materials*, 174(1-3), 694-699.

Castiglioni, S., Bagnati, R., Fanelli, R., Pomati, F., Calamari, D., & Zuccato, E. (2006). Removal of pharmaceuticals in sewage treatment plants in Italy. *Environmental Science & Technology*, 40(1), 357-363.

Chalew, T. E., & Halden, R. U. (2009). Environmental exposure of aquatic and terrestrial biota to triclosan and triclocarban 1. *JAWRA Journal of the American Water Resources Association*, *45*(1), 4-13.

Chander Sharma, P., Yadav, S., Pahwa, R., Sharma, A., & Jain, S. (2011). Naproxen: an update on physicochemical, analytical and pharmacological aspects. *Anti-Inflammatory & Anti-Allergy Agents in Medicinal Chemistry (Formerly Current Medicinal Chemistry-Anti-Inflammatory and Anti-Allergy Agents), 10*(5), 339-350.

Chanzu, H. A., Onyari, J. M., & Shiundu, P. M. (2012). Biosorption of malachite green from aqueous solutions onto polylactide/spent brewery grains films: kinetic and equilibrium studies. *Journal of Polymers and the Environment,* 20(3), 665-672.

Chequer, F. M. D., Lizier, T. M., de Felício, R., Zanoni, M. V. B., Debonsi, H. M., &de Oliveira, D. P. (2011). Analyses of the genotoxic and mutagenic potential of the products formed after the biotransformation of the azo dye Disperse Red 1. *Toxicology in Vitro,* 25(8), 2054-2063.

Choudhary, M., Jetley, U. K., Khan, M. A., Zutshi, S., & Fatma, T. (2007). Effect of heavy metal stress on proline, malondialdehyde, and superoxide dismutase activity in the cyanobacterium Spirulina platensis-S5. *Ecotoxicology and environmental safety,* 66(2), 204-209.

Choudhury, A. K. R. (2018). Eco-friendly dyes and dyeing. *Advanced Materials and Technologies for Environmental*, *2,* 145-76.

Clara, M., Strenn, B., Gans, O., Martinez, E., Kreuzinger, N., & Kroiss, H. (2005). Removal of selected pharmaceuticals, fragrances and endocrine disrupting compounds in a membrane bioreactor and conventional wastewater treatment plants. *Water research,* 39(19), 4797-4807.

Cornelissen, G., Gustafsson, Ö., Bucheli, T. D., Jonker, M. T., Koelmans, A. A., & van Noort, P. C. (2005). Extensive sorption of organic compounds to black carbon, coal, and kerogen in sediments and soils: mechanisms and consequences for distribution, bioaccumulation, and biodegradation. *Environmental science & technology,* 39(18), 6881-6895.

Cosgrove, W. J., & Loucks, D. P. (2015). Water management: Current and future challenges and research directions. *Water Resources Research*, *51*(6), 4823-4839.

Cosgrove, W. J., & Loucks, D. P. (2015). Water management: Current and future challenges and research directions. *Water Resources Research*, *51*(6), 4823-4839.

Crini, G. (2006). Non-conventional low-cost adsorbents for dye removal: a review. *Bioresource technology*, 97(9), 1061-1085.

Crini, G., Lichtfouse, E., Wilson, L. D., & Morin-Crini, N. (2019). Conventional and non-conventional adsorbents for wastewater treatment. *Environmental Chemistry Letters*, *17*(1), 195-213.

Cuevas, N., Zorita, I., Costa, P. M., Franco, J., & Larreta, J. (2015). Development of histopathological indices in the digestive gland and gonad of mussels: integration with contamination levels and effects of confounding factors. *Aquatic toxicology*, *162*, 152-164.

Da Silva, C. M., Da Silva, D. L., Modolo, L. V., Alves, R. B., de Resende, M. A., Martins, C. V., & de Fatima, A. (2011). Schiff bases: A short review of their antimicrobial activities. *Journal of Advanced research*, 2(1), 1-8.

Dasgupta, J., Sikder, J., Chakraborty, S., Curcio, S., & Drioli, E. (2015). Remediation of textile effluents by membrane-based treatment techniques: a state-of-the-art review. *Journal of environmental management*, 147, 55-72.

Dawood, S., & Sen, T. K. (2012). Removal of anionic dye Congo red from aqueous solution by raw pine and acid-treated pine cone powder as adsorbent: equilibrium, thermodynamic, kinetics, mechanism and process design. *Water research,* 46(6), 1933-1946.

De Souza, A. P. N., Licea, Y. E., Colaço, M. V., Senra, J. D., & Carvalho, N. M. (2021). Green iron oxides/amino-functionalized MCM-41 composites as adsorbent for anionic azo dye: Kinetic and isotherm studies. *Journal of Environmental Chemical Engineering*, *9*(2), 105062.

Dhillon, G. S., Kaur, S., Pulicharla, R., Brar, S. K., Cledón, M., Verma, M., & Surampalli, R. Y. (2015). Triclosan: current status, occurrence, environmental risks and bioaccumulation potential. *International journal of environmental research and public health*, *12*(5), 5657-5684.

Dobrin, D., Magureanu, M., Bradu, C., Mandache, N. B., & Parvulescu, V. I. (2014, May). Combination of non-thermal plasma and ozonation for the degradation of endocrine disrupting compounds in water. In *2014 International Conference on Optimization of Electrical and Electronic Equipment (OPTIM)* (pp. 1047-1052). IEEE.

Dossey, A. T. (2010). Insects and their chemical weaponry: new potential for drug discovery. *Natural product reports*, *27*(12), 1737-1757.

Dufresne, A. (2010). Polymer nanocomposites from biological sources. *Encyclopedia of nanoscience and nanotechnology*, 219-250.

El Qada, E. N., Allen, S. J., & Walker, G. M. (2008). Adsorption of basic dyes from aqueous solution onto activated carbons. *Chemical Engineering Journal*, 135(3), 174-184.

Ellis, J. B. (2006). Pharmaceutical and personal care products (PPCPs) in urban receiving waters. *Environmental pollution*, 144(1), 184-189.

Errais, E., Duplay, J., Darragi, F., M'Rabet, I., Aubert, A., Huber, F., & Morvan, G. (2011). Efficient anionic dye adsorption on natural untreated clay: Kinetic study and thermodynamic parameters. *Desalination*, *275*(1-3), 74-81.

Faisal, S. (2013). *Synthesis of multifunctional reactive dyes and their application onto wool fabric by inkjet printing*. University of Leeds.

Farooq, U., Khan, M. A., Athar, M., & Kozinski, J. A. (2011). Effect of modification of environmentally friendly biosorbent wheat (Triticum aestivum) on the biosorptive removal of cadmium (II) ions from aqueous solution. *Chemical engineering journal*, *171*(2), 400-410.

Farshid G., Ali M.S., Maryam, M., (2015) Production of Silica Nanoparticles from Rice Husk as Agricultural Waste by Environmentally Friendly Technique. *Environmental Studies of Persian Gulf,* 2(1)56-65

Fu J, Chen Z, Wang M, Liu S, Zhang J, Zhang J, Xu Q (2015) Adsorption of methylene blue by a high-efficiency adsorbent (polydopamine microspheres): kinetics, isotherm, thermodynamics and mechanism analysis. *Chem Eng J* 259: 53–61. 10.1016/j.cej.2014.07.101

Fu, Y., & Viraraghavan, T. (2001). Fungal decolorization of dye wastewaters: a review. *Bioresource technology*, 79(3), 251-262.

Garg, D. (2012). *Adsorptive removal of dyes from aqueous solution using Cu-BTC and Commercial Activated Carbon* (Doctoral dissertation).

Golka, K., Sondermann, R., Reich, S. E., & Wiese, A. (2004). Carbohydrate-deficient transferrin (CDT) as a biomarker in persons suspected of alcohol abuse. *Toxicology letters*, 151(1), 235-241.

Gonzalez-Rey, M., Tapie, N., Le Menach, K., Devier, M. H., Budzinski, H., & Bebianno, M. J. (2015). Occurrence of pharmaceutical compounds and pesticides in aquatic systems. *Marine Pollution Bulletin*, *96*(1-2), 384-400.

Goswami, M., & Phukan, P. (2017). Enhanced adsorption of cationic dyes using sulfonic acid modified activated carbon. *Journal of Environmental Chemical Engineering*, *5*(4), 3508-3517.

Gupta, V. K., Carrott, P. J. M., Ribeiro Carrott, M. M. L., & Suhas. (2009). Low-cost adsorbents: growing approach to wastewater treatment—a review. Critical Reviews in *Environmental Science and Technology*, 39(10), 783-842.

Haman, C., Dauchy, X., Rosin, C., & Munoz, J. F. (2015). Occurrence, fate and behavior of parabens in aquatic environments: a review. *Water Research*, *68*, 1-11.

Hameed, B. H. (2009). Spent tea leaves: a new non-conventional and low-cost adsorbent for removal of basic dye from aqueous solutions. *Journal of hazardous materials*, *161*(2-3), 753-759.

Han, R., Wang, Y., Sun, Q., Wang, L., Song, J., He, X., & Dou, C. (2010). Malachite green adsorption onto natural zeolite and reuse by microwave irradiation. *Journal of Hazardous Materials*, *175*(1-3), 1056-1061.

Hanafiah, Z. M., Mohtar, W. H. M. W., Abd Manan, T. S. B., Bachi, N. A., Abdullah, N. A., Abd Hamid, H. H., & Rasdi, N. W. (2022). The occurrence of non-steroidal anti-inflammatory drugs (NSAIDs) in Malaysian urban domestic wastewater. *Chemosphere*, *287*, 132134.

Haris, M. R. H. M., Wahab, N. A. A., Reng, C. W., Azahari, B., & Sathasivam, K. (2011). The sorption of cadmium (II) ions on mercerized rice husk and activated carbon. Turkish *Journal of Chemistry,* 35(6), 939-950.

Hena, S., Gutierrez, L., & Croué, J. P. (2021). Removal of pharmaceutical and personal care products (PPCPs) from wastewater using microalgae: A review. *Journal of hazardous materials, 403*, 124041.

Houe, R., & Grabot, B. (2009). Assessing the compliance of a product with an eco-label: From standards to constraints. International *Journal of Production Economics,* 121(1), 21-38.

Iacopetta, D., Catalano, A., Ceramella, J., Saturnino, C., Salvagno, L., Ielo, I., & Sinicropi, M. S. (2021). The different facets of triclocarban: A review. *Molecules*, *26*(9), 2811.

Inyinbor AA, Adekola FA, Olatunji GA (2016) Kinetics, isotherms and thermodynamic modeling of liquid phase adsorption of Rhodamine B dye onto Raphiahookerie fruit epicarp. *Water Resource Ind*15: 14–27. 10.1016/j.wri.2016.06.001

Jain, R., Mathur, M., Sikarwar, S., & Mittal, A. (2007). Removal of the hazardous dye rhodamine B through photocatalytic and adsorption treatments. *Journal of Environmental Management,* 85(4), 956-964.

Jain, S., & Jain, P. K. (2020). Classification, chemistry, and applications of chemical substances that are harmful to the environment: Classification of dyes. In *Impact of textile dyes on public health and the environment* (pp. 20-49). IGI Global.

Jaishankar, M., Tseten, T., Anbalagan, N., Mathew, B. B., & Beeregowda, K. N. (2014). Toxicity, mechanism and health effects of some heavy metals. *Interdisciplinary toxicology, 7*(2), 60.

Jamaly, S., Darwish, N. N., Ahmed, I., & Hasan, S. W. (2014). A short review on reverse osmosis pretreatment technologies. *Desalination*, 354, 30-38.

Jodeh, S., Abdelwahab, F., Jaradat, N., Warad, I., & Jodeh, W. (2016). Adsorption of diclofenac from aqueous solution using Cyclamen persicum tubers based activated carbon (CTAC). *Journal of the Association of Arab Universities for Basic and Applied Sciences*, *20*, 32-38.

Johnson, A. C., Jürgens, M. D., Williams, R. J., Kümmerer, K., Kortenkamp, A., & Sumpter, J. P. (2008). Do cytotoxic chemotherapy drugs discharged into rivers pose a risk to the environment and human health? An overview and UK case study. *Journal of Hydrology, 348*(1-2), 167-175.

Johnson, W., & Bouchard Jr, T. J. (2005). Constructive replication of the visual–perceptual-image rotation model in Thurstone's (1941) *battery of 60 tests of mental ability. Intelligence,* 33(4), 417-430.

Kadam, S. U., Tiwari, B. K., & O'Donnell, C. P. (2013). Application of novel extraction technologies for bioactives from marine algae. *Journal of agricultural and food chemistry*, 61(20), 4667-4675.

Karaman, R., Khamis, M., Quried, M., Halabieh, R., Makharzeh, I., Manassra, A., & Nir, S. (2012). Removal of diclofenac potassium from wastewater using clay-micelle complex. *Environmental technology,* 33(11), 1279-1287.

Katheresan, V., Kansedo, J., & Lau, S. Y. (2018). Efficiency of various recent wastewater dye removal methods: A review. *Journal of environmental chemical engineering, 6*(4), 4676-4697.

Kayranli, B. (2011). Adsorption of textile dyes onto iron-based waterworks sludge from aqueous solution, isotherm, kinetic and thermodynamic study. *Chemical engineering journal*, *173*(3), 782-791.

Khairiraihanna, J., Norasikin, S., Song, S., & Hanapi, M. (2015). Adsorption equilibrium and kinetics of elemental mercury onto Coconut Pith. *Journal of Environmental Science and Technology*, *8*(2), 74-82.

Khataee, A. R., Vafaei, F., & Jannatkhah, M. (2013). Biosorption of three textile dyes from contaminated water by filamentous green algal *Spirogyra sp*.: Kinetic, isotherm and thermodynamic studies. *International Biodeterioration & Biodegradation,* 83, 33-40.

Khatri, A., Peerzada, M. H., Mohsin, M., & White, M. (2015). A review on developments in dyeing cotton fabrics with reactive dyes for reducing effluent pollution. *Journal of Cleaner Production*, *87*, 50-57.

Khatri, A., Peerzada, M. H., Mohsin, M., & White, M. (2015). A review on developments in dyeing cotton fabrics with reactive dyes for reducing effluent pollution. *Journal of Cleaner Production*, *87*, 50-57.

Khilchevskyi, V., & Karamushka, V. (2021). Global Water Resources: Distribution and Demand. In *Clean Water and Sanitation* (pp. 1-11). Cham: Springer International Publishing.

Khilchevskyi, V., & Karamushka, V. (2021). Global Water Resources: Distribution and Demand. In *Clean Water and Sanitation* (pp. 1-11). Cham: Springer International Publishing.

Kithiia, J. (2011). Climate change risk responses in East African cities: need, barriers and opportunities. *Current opinion in environmental sustainability,* 3(3), 176-180.

Koh, J. (2011). Dyeing with disperse dyes. *Textile dyeing*, *10*, 195-220.

Kolpin, D. W., Furlong, E. T., Meyer, M. T., Thurman, E. M., Zaugg, S. D., Barber, L. B., & Buxton, H. T. (2002). Pharmaceuticals, hormones, and other organic wastewater contaminants in US streams, 1999− 2000: A national reconnaissance. *Environmental science & technology*, 36(6), 1202-1211.

Kümmerer, K. (2010). Pharmaceuticals in the environment. Annual review of *environment and resources*, 35, 57-75.

Kurniawan, T. A., Chan, G. Y., Lo, W. H., & Babel, S. (2006). Physio–chemical treatment techniques for wastewater laden with heavy metals. *Chemical engineering journal*, 118(1-2), 83-98.

Kyzas, George Z., et al. "New approaches on the removal of pharmaceuticals from wastewaters with adsorbent materials. *Journal of molecular liquids* 209 (2015): 87-93.

Leboda R (1992). Carbon-mineral adsorbents — new type of sorbents? Part I. The methods of preparation. *Materials Chemistry and Physics*, 31: 243-255.

Leboda R, Charmas B, Chodorowski S, Skubiszewska-Zięba J, Gun’ko VM (2006). Improved carbon mineral adsorbents derived from cross-linking carbon-bearing residues in spent palygorskite. *Microporous and Mesoporous Materials*, 87: 207-216.

Leone, V. O., Pereira, M. C., Aquino, S. F. D., Oliveira, L. C. A. D., Corrêa, S., Ramalho, T. D. C., & Silva, A. C. D. (2018). Adsorption of diclofenac on a magnetic adsorbent based on maghemite: experimental and theoretical studies. *New Journal of Chemistry*, 42(1), 437-449.

Li, W., Mu, B., & Yang, Y. (2019). Feasibility of industrial-scale treatment of dye wastewater via bio-adsorption technology. *Bioresource Technology*, *277*, 157-170.

Lodeiro, I. G., Macphee, D. E., Palomo, A., & Fernández-Jiménez, A. (2009). Effect of alkalis on fresh C–S–H gels. FTIR analysis. *Cement and Concrete Research*, *39*(3), 147-153.

Lu, L., Sun, M., Lu, Q., Wu, T., & Huang, B. (2021). High energy X-ray radiation sensitive scintillating materials for medical imaging, cancer diagnosis and therapy. *Nano Energy*, *79*, 105437.

Lu, X., Shao, Y., Gao, N., Chen, J., Zhang, Y., Wang, Q., & Lu, Y. (2016). Adsorption and removal of clofibric acid and diclofenac from water with MIEX resin. *Chemosphere*, *161*, 400-411.

Ma, J., Yu, F., Zhou, L., Jin, L., Yang, M., Luan, J., & Chen, J. (2012). Enhanced adsorptive removal of methyl orange and methylene blue from aqueous solution by alkali-activated multiwalled carbon nanotubes. *ACS applied materials & interfaces*, *4*(11), 5749-5760.

Maeda, N., Shimomura, I., Kishida, K., Nishizawa, H., Matsuda, M., Nagaretani, & Komuro, R. (2002). Diet-induced insulin resistance in mice lacking adiponectin/ACRP30. *Nature medicine*, 8(7), 731

Mailler, R., Gasperi, J., Coquet, Y., Deshayes, S., Zedek, S., Cren-Olivé, C., & Rocher, V. (2015). Study of a large scale powdered activated carbon pilot: Removals of a wide range of emerging and priority micropollutants from wastewater treatment plant effluents. *Water Research*, *72*, 315-330.

Majid, M., Masoud, R.,Mohammad, H. A., and Vahid, M. (2014). Synthesis and Characterization of Nano SiO_2 from Rice Husk Ash by Precipitation Method. *3rd National Conference on Modern Researches in Chemistry and Chemical Engineering*

Malato, S., Fernández-Ibáñez, P., Maldonado, M. I., Blanco, J., & Gernjak, W. (2009). Decontamination and disinfection of water by solar photocatalysis: recent overview and trends. *Catalysis today*, 147(1), 1-59.

Mane, V. S., & Babu, P. V. (2013). Kinetic and equilibrium studies on the removal of Congo red from aqueous solution using Eucalyptus wood (Eucalyptus globulus) saw dust. *Journal of the Taiwan Institute of Chemical Engineers*, 44(1), 81-88.

Marras, S. (2015). Application of advanced methodologies to the identification of natural dyes and lakes in pictorial artworks.

Mazumder, M., Ahmed, R., Ali, A. W., & Lee, S. J. (2018). SEM and ESEM techniques used for analysis of asphalt binder and mixture: A state of the art review. *Construction and Building Materials*, *186*, 313-329.

Meride, Y., & Ayenew, B. (2016). Drinking water quality assessment and its effects on residents' health in Wondo genet campus, Ethiopia. *Environmental Systems Research*, *5*(1), 1-7.

Mijangos, L., Ziarrusta, H., Olivares, M., Zuloaga, O., Möder, M., Etxebarria, N., & Prieto, A. (2018). Simultaneous determination of 41 multiclass organic pollutants in environmental waters by means of polyethersulfone microextraction followed by liquid chromatography–tandem mass spectrometry. *Analytical and bioanalytical chemistry*, *410*(2), 615-632.

Modi, K., Paterek, T., Son, W., Vedral, V., & Williamson, M. (2010). Unified view of quantum and classical correlations. *Physical review letters*, 104(8), 080501.

Mompelat, S., Le Bot, B., & Thomas, O. (2009). Occurrence and fate of pharmaceutical products and by-products, from resource to drinking water. *Environment international*, *35*(5), 803-814.

Morin, J. F. (2017). Recent advances in the chemistry of vat dyes for organic electronics. *Journal of Materials Chemistry C*, *5*(47), 12298-12307.

Mukherjee, K., Saha, R., Ghosh, A., & Saha, B. (2013). Chromium removal technologies. *Research on Chemical Intermediates,* 39(6), 2267-2286.

Nawrocka, D., & Parker, T. (2009). Finding the connection: environmental management systems and environmental performance. *Journal of Cleaner Production,* 17(6), 601-607.

Nieto-Juárez, J. I., Torres-Palma, R. A., Botero-Coy, A. M., & Hernández, F. (2021). Pharmaceuticals and environmental risk assessment in municipal wastewater treatment plants and rivers from Peru. *Environment International, 155,* 106674.

Opanga, M. A. (2018). *Assessment of Selected Antibiotics in Ngong River and Their Removal Using Activated Carbon* (Doctoral dissertation, University of Nairobi).

Osorio, V., Cruz-Alcalde, A., & Pérez, S. (2022). Nitrosation and nitration of diclofenac and structurally related nonsteroidal anti-inflammatory drugs (NSAIDs) in nitrifying activated sludge. *Science of The Total Environment, 807*, 150533.

Oyekanmi, A. A., Ahmad, A., Hossain, K., & Rafatullah, M. (2019). Adsorption of Rhodamine B dye from aqueous solution onto acid treated banana peel: Response surface methodology, kinetics and isotherm studies. *PLoS One,14*(5), e0216878.

Pandey, A., Singh, P., & Iyengar, L. (2007). Bacterial decolorization and degradation of azo dyes. *International biodeterioration & biodegradation,* 59(2), 73-84.

Parolini, M. (2020). Toxicity of the Non-Steroidal Anti-Inflammatory Drugs (NSAIDs) acetylsalicylic acid, paracetamol, diclofenac, ibuprofen and naproxen towards freshwater invertebrates: A review. *Science of the Total Environment*, *740*, 140043.

Parolini, M. (2020). Toxicity of the Non-Steroidal Anti-Inflammatory Drugs (NSAIDs) acetylsalicylic acid, paracetamol, diclofenac, ibuprofen and naproxen towards freshwater invertebrates: A review. *Science of the Total Environment*, *740*, 140043.

Patel, S. (2012). Potential of fruit and vegetable wastes as novel biosorbents: summarizing the recent studies. Reviews in *Environmental Science and Biotechnology,* 11(4), 365-380.

Patra, T., Mohanty, A., Singh, L., Muduli, S., Parhi, P. K., & Sahoo, T. R. (2022). Effect of calcination temperature on morphology and phase transformation of MnO2 nanoparticles: A step towards green synthesis for reactive dye adsorption. *Chemosphere*, *288*, 132472.

Pereira, A. L., de Vasconcelos Barros, R. T., & Pereira, S. R. (2017). Pharmaco pollution and Household Waste Medicine (HWM): how reverse logistics is environmentally important to Brazil. *Environmental Science and Pollution Research*, *24*(31), 24061-24075.

Pode, R. (2016). Potential applications of rice husk ash waste from rice husk biomass power plant. *Renewable and Sustainable Energy Reviews*, *53,* 1468-1485.

Pode, R. (2016). Potential applications of rice husk ash waste from rice husk biomass power plant. *Renewable and Sustainable Energy Reviews*, *53,* 1468-1485.

Pourjavadi, A., Nazari, M., Kabiri, B., Hosseini, S. H., & Bennett, C. (2016). Preparation of porous graphene oxide/hydrogel nanocomposites and their ability for efficient adsorption of methylene blue. *RSC advances*, *6*(13), 10430-10437.

Prajwal, S., Vasudevan, V. N., Sathu, T., Irshad, A., Nayankumar, S. R., & Pame, K. (2017). Antibiotic residues in food animals: Causes and health effects. *The Pharma Innovation Journal*, *6*(12), 01-04.

Putyera K, Bandosz TJ, Jagiello J, Schwarz JA (1994). Sorption properties of carbon composite materials formed from layered clay minerals. Clays and clay minerals, 42: 1-6. in textile effluent: a critical review on current treatment technologies with a proposed alternative. *Bioresource Technology,* 77, 247-255.

Rajesh, Y., Nita, Y., & Dhar, K. M. (2014). A review: Dye yielding sources and their importance. *International Journal of Pharmacognosy and Phytochemical Research*, *6*(2), 241-248.

Ramezanianpour, A. A., Mahdikhani, M., & Ahmadibeni, G. H. (2009). The effect of rice husk ash on mechanical properties and durability of sustainable concretes.

Rangsayatorn, N., Pokethitiyook, P., Upatham, E. S., & Lanza, G. R. (2004). Cadmium biosorption by cells of Spirulina platensis TISTR 8217 immobilized in alginate and silica gel. *Environment International*, 30(1), 57-63.

Rao, M. M., Ramesh, A., Rao, G. P. C., & Seshaiah, K. (2006). Removal of copper and cadmium from the aqueous solutions by activated carbon derived from Ceiba pentandra hulls. *Journal of hazardous materials*, *129*(1-3), 123-129.

Ritter, Keith Solomon, Paul Sibley, Ken Hall, Patricia Keen, Gevan Mattu, Beth Linton, L. (2002). Sources, pathways, and relative risks of contaminants in surface water and groundwater: a perspective prepared for the Walkerton inquiry. *Journal of Toxicology and Environmental Health Part A*, *65*(1), 1-142.

Ritter, Keith Solomon, Paul Sibley, Ken Hall, Patricia Keen, Gevan Mattu, Beth Linton, L. (2002). Sources, pathways, and relative risks of contaminants in surface water and groundwater: a perspective prepared for the Walkerton inquiry. *Journal of Toxicology and Environmental Health Part A*, *65*(1), 1-142.

Robinson, T., McMullan, G., Marchant, R., & Nigam, P. (2001). Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. *Bioresource technology*, 77(3), 247-255.

Safa, Y., & Bhatti, H. N. (2011). Kinetic and thermodynamic modeling for the removal of Direct Red-31 and Direct Orange-26 dyes from aqueous solutions by rice husk. *Desalination*, 272(1-3), 313-322.

Sahu, O., Mazumdar, B., & Chaudhari, P. K. (2014). Treatment of wastewater by electrocoagulation: a review. *Environmental science and pollution research*, 21(4), 2397-2413.

Salvestrini, S., Fenti, A., Chianese, S., Iovino, P., & Musmarra, D. (2020). Diclofenac sorption from synthetic water: Kinetic and thermodynamic analysis. *Journal of Environmental Chemical Engineering*, *8*(5), 104105.

Sandeman, S. R., Gun’ko, V. M., Bakalinska, O. M., Howell, C. A., Zheng, Y., Kartel, M. T., & Mikhalovsky, S. V. (2011). Adsorption of anionic and cationic dyes by activated carbons, PVA hydrogels, and PVA/AC composite. *Journal of colloid and interface science*, *358*(2), 582-592.

Sannino, F., Ruocco, S., Marocco, A., Esposito, S., & Pansini, M. (2012). Cyclic process of simazine removal from waters by adsorption on zeolite HY and its regeneration by thermal treatment. *Journal of hazardous materials*, 229, 354-360.

Santos, L. H., Gros, M., Rodriguez-Mozaz, S., Delerue-Matos, C., Pena, A., Barceló, D., & Montenegro, M. C. B. (2013). Contribution of hospital effluents to the load of pharmaceuticals in urban wastewaters: identification of ecologically relevant pharmaceuticals. *Science of the Total Environment*, *461*, 302-316.

Saratale, R. G., Saratale, G. D., Chang, J. S., & Govindwar, S. P. (2011). Bacterial decolorization and degradation of azo dyes: a review. *Journal of the Taiwan Institute of Chemical Engineers*, 42(1), 138-157.

Schwarzenbach, R. P., Egli, T., Hofstetter, T. B., Von Gunten, U., & Wehrli, B. (2010). Global water pollution and human health. Annual Review of *Environment and Resources*, 35, 109-136.

Sengar, A., & Vijayanandan, A. (2022). Human health and ecological risk assessment of 98 pharmaceuticals and personal care products (PPCPs) detected in Indian surface and wastewaters. *Science of the Total Environment*, *807*, 150677.

Shan RR, Yan LG, Yang YM, Yang K, Yu SJ, Yu HQ, et al. (2015) Highly efficient removal of three red dyes by adsorption onto Mg–Al-layered double hydroxide. *J Ind Eng Chem* 21: 561–568. 10.1016/j.jiec.2014.03.019

Shannon, M. A., Bohn, P. W., Elimelech, M., Georgiadis, J. G., Marinas, B. J., & Mayes, A. M. (2010). Science and technology for water purification in the coming decades in Nanoscience and Technology: A Collection of Reviews from *Nature Journals* (pp. 337-346).

Shore, R. F., Taggart, M. A., Smits, J., Mateo, R., Richards, N. L., & Fryday, S. (2014). Detection and drivers of exposure and effects of pharmaceuticals in higher vertebrates. Philosophical Transactions of the Royal Society B: *Biological Sciences,* 369(1656), 20130570.

Singh K, Arora S (2011). Removal of Synthetic Textile Dyes from Wastewaters: A Critical Review on Present Treatment Technologies. Critical Reviews in *Environmental Science and Technology,* 41: 807-878.

Singh, K., & Arora, S. (2011). Removal of synthetic textile dyes from wastewaters: a critical review on present treatment technologies. Critical reviews in *environmental science and technology*, 41(9), 807-878.

Ślósarczyk, K., Jakóbczyk-Karpierz, S., Różkowski, J., & Witkowski, A. J. (2021). Occurrence of pharmaceuticals and personal care products in the water environment of Poland: a review. *Water, 13*(16), 2283.

Ślósarczyk, K., Jakóbczyk-Karpierz, S., Różkowski, J., & Witkowski, A. J. (2021). Occurrence of pharmaceuticals and personal care products in the water environment of Poland: a review. *Water, 13*(16), 2283.

Springfield, T. (2011). *Application of FTIR for Quantification of Alkali in Cement*. University of North Texas.

Steter, J. R., Brillas, E., & Sirés, I. (2016). On the selection of the anode material for the electrochemical removal of methylparaben from different aqueous media. *Electrochimica Acta, 222*, 1464-1474.

Stolz, A. (2001). Basic and applied aspects in the microbial degradation of azo dyes. *Applied microbiology and biotechnology*, 56(1-2), 69-80.

Sulyman, M., Al-Marog, S., Al-Azabi, K., Dawed, E., & Abukrain, A. (2020). Economical and eco-friendly adsorbent derived from coffee waste for efficient adsorption of methylene blue: Characterization, evaluation and optimization studies. *Chem. Sci. Int. J, 29*(10), 16-36.

Syed Fariq Fathullah, S. Y. (2019). *Magnetic sporopollenin based cyclodextrin and calixarene: Molecular modelling, characterization and application for determination of non-steroidal anti-inflammatory drugs/Syed Fariq Fathullah Syed Yaacob* (Doctoral dissertation, Universiti Malaya).

Szychowski D, Pacewska B (2012). Methods of preparation and properties of mineral-carbon sorbents mobtained from coal-tar pitch-polymer compositions. *Journal of Thermal Analysis and Calorimetry*, 109: 789-795.

Tang, Y., Zhong, Y., Li, H., Huang, Y., Guo, X., Yang, F., & Wu, Y. (2020). Contaminants of emerging concern in aquatic environment: occurrence, monitoring, fate, and risk assessment. *Water Environment Research*, *92*(10), 1811-1817.

Thirunavukkarasu, A., & Nithya, R. (2020). Adsorption of acid orange 7 using green synthesized CaO/CeO_2 composite: an insight into kinetics, equilibrium, thermodynamics, mass transfer and statistical models. *Journal of the Taiwan Institute of Chemical Engineers*, *111*, 44-62.

Thomaidi, Vasiliki S., Christos Matsoukas, and Athanasios S. Stasinakis. "Risk assessment of triclosan released from sewage treatment plants in European rivers using a combination of risk quotient methodology and Monte Carlo simulation. *Science of the Total Environment* 603 (2017): 487-494.

Tian, X., Zhu, H., Meng, X., Wang, J., Zheng, C., Xia, Y., & Xiong, Z. (2020). Amphiphilic calcium alginate carbon aerogels: broad-spectrum adsorbents for ionic and solvent dyes with multiple functions for decolorized oil–water separation. *ACS Sustainable Chemistry & Engineering*, *8*(34), 12755-12767.

Tiwari, B., Sellamuthu, B., Ouarda, Y., Drogui, P., Tyagi, R. D., & Buelna, G. (2017). Review on fate and mechanism of removal of pharmaceutical pollutants from wastewater using biological approach. *Bioresource technology*, *224*, 1-12.

Tripathi, A., & Rai, A. K. (2022). Chemicals Utilised in Industries of Food and Textile Dyes, Their Effects and Treatment. *Central Asian Journal of Theoretical and Applied Science*, *3*(7), 42-52.

Tuck, M., Blanc, L., Touti, R., Patterson, N. H., Van Nuffel, S., Villette, S., & Desbenoit, N. (2020). Multimodal imaging based on vibrational spectroscopies and mass spectrometry imaging applied to biological tissue: a multiscale and multiomics review. *Analytical chemistry*, *93*(1), 445-477.

Ţucureanu, V., Matei, A., & Avram, A. M. (2016). FTIR spectroscopy for carbon family study. *Critical reviews in analytical chemistry*, *46*(6), 502-520.

UNDP (2009). Protecting Pacific Island children and women during economic and food crises: Working Edition One for advocacy, debate and guidance.

UNDP, H. (2005). Democracy in Latin America: Towards a citizens’ democracy. New York, USA

UNDP, H. (2007). Human development report 2007/2008. Fighting climate change: Human solidarity in a divided world. Human development report.

UNEP (2008) UN collaborative programme on reducing emissions from deforestation and forest degradation in development countries (UN-REDD) framework document; van der werf. GR, Morton, DC, DeFries, RS, Olivier, JG, Kasibhatla, PS, Jackson, RB, Collatz, JG and Randerson, JT, 737-738.

Van der Bruggen, B., Vandecasteele, C., Van Gestel, T., Doyen, W., & Leysen, R. (2003). A review of pressure-driven membrane processes in wastewater treatment and drinking water production. *Environmental progress*, 22(1), 46-56.

Varjani, S. J., & Chaithanya Sudha, M. (2018). Treatment technologies for emerging organic contaminants removal from wastewater. In *Water remediation* (pp. 91-115). Springer, Singapore.

Velusamy, S., Roy, A., Sundaram, S., & Kumar Mallick, T. (2021). A review on heavy metal ions and containing dyes removal through graphene oxide-based adsorption strategies for textile wastewater treatment. *The Chemical Record, 21*(7), 1570-1610.

Velusamy, S., Roy, A., Sundaram, S., & Kumar Mallick, T. (2021). A review on heavy metal ions and containing dyes removal through graphene oxide-based adsorption strategies for textile wastewater treatment. *The Chemical Record, 21*(7), 1570-1610.

Venegas, M., Leiva, A. M., Reyes-Contreras, C., Neumann, P., Piña, B., & Vidal, G. (2021). Presence and fate of micropollutants during anaerobic digestion of sewage and their implications for the circular economy: A short review. *Journal of Environmental Chemical Engineering*, *9*(1), 104931.

Vijayasarathy, P. R. (2018). *Engineering chemistry*. PHI Learning Pvt. Ltd.

Vučurović, V. M., Razmovski, R. N., & Tekić, M. N. (2012). Methylene blue (cationic dye) adsorption onto sugar beet pulp: equilibrium isotherm and kinetic studies. *Journal of the Taiwan Institute of Chemical Engineers*, *43*(1), 108-111.

Wang, J., & Wang, S. (2016). Removal of pharmaceuticals and personal care products (PPCPs) from wastewater: a review. *Journal of environmental management, 182*, 620-640.

Wang, J., Su, Y., Lv, S. W., & Sun, L. H. (2022). The efficient removal of diclofenac sodium and bromocresol green from aqueous solution by sea urchin-like Ni/Co-BTC bimetallic organic framework: adsorption isotherms, kinetics and mechanisms. *New Journal of Chemistry*, *46*(38), 18374-18383.

Wang, S., & Peng, Y. (2010). Natural zeolites as effective adsorbents in water and wastewater treatment. *Chemical Engineering Journal*, 156(1), 11-24.

Wato, T., Amare, M., Bonga, E., Demand, B. B. O., & Coalition, B. B. R. (2020). The agricultural water pollution and its minimization strategies–A review. *J. Resour. Dev. Manag*, *64*, 10-22.

Wato, T., Amare, M., Bonga, E., Demand, B. B. O., & Coalition, B. B. R. (2020). The agricultural water pollution and its minimization strategies–A review. *J. Resour. Dev. Manag*, *64*, 10-22.

Weinberg, B. A., & Bealer, B. K. (2004). Caffeine and health. In *Beverages in Nutrition and Health* (pp. 171-185). Humana Press, Totowa, NJ.

Wesenberg, D., Kyriakides, I., & Agathos, S. N. (2003). White-rot fungi and their enzymes for the treatment of industrial dye effluents. Biotechnology advances, 22(1-2), 161-187.

Yang N, Zhu S, Zhang D, Xu S (2008). Synthesis and properties of magnetic Fe3O4-activated carbon nanocomposite particles for dye removal. Materials Letters, 62: 645-647.

Yang, H., Yan, R., Chen, H., Lee, D. H., & Zheng, C. (2007). Characteristics of hemicellulose, cellulose and lignin pyrolysis. *Fuel*, *86*(12-13), 1781-1788.

Zekker, I. (2022). Editorial to Efficient Catalytic and Microbial Treatment of Water Pollutants. *Water*, *14*(6), 995.

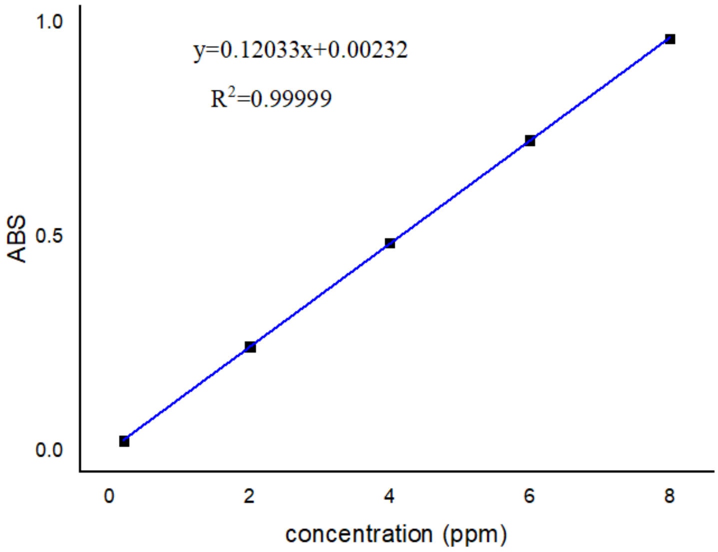
Zhao, Y., Liu, F., & Qin, X. (2019). Removal of diclofenac from aqueous phase by birnessite: effects of pH and common ions. *Water, Air, & Soil Pollution*, *230*(1), 1-11.

Zhu HY, Fu YQ, Jiang R, Jiang JH, Xiao L, Zeng GM, Zhao SL, Wang Y (2011a). Adsorption removal of congo red onto magnetic cellulose/Fe3O4/activated carbon composite: Equilibrium, kinetic and thermodynamic studies. Chemical Engineering Journal, 173: 494-502.

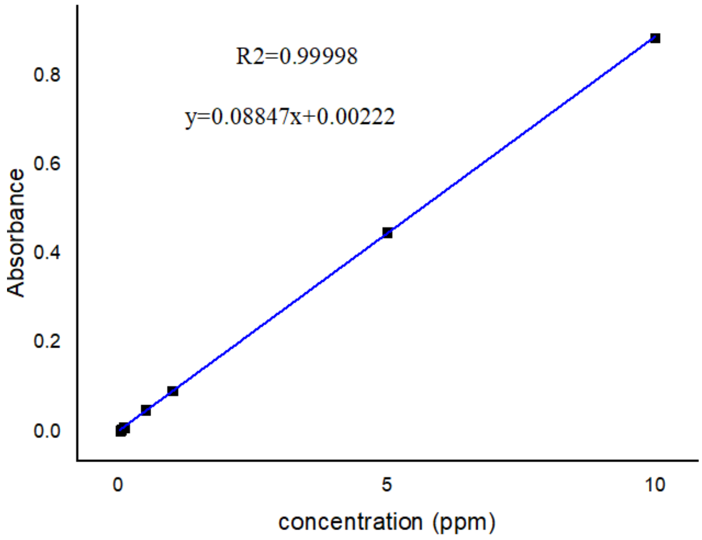
Zunngu, S. S., Madikizela, L. M., Chimuka, L., & Mdluli, P. S. (2017). Synthesis and application of a molecularly imprinted polymer in the solid-phase extraction of ketoprofen from wastewater. *Comptes Rendus Chimie*, *20*(5), 585-591.

APPENDICES

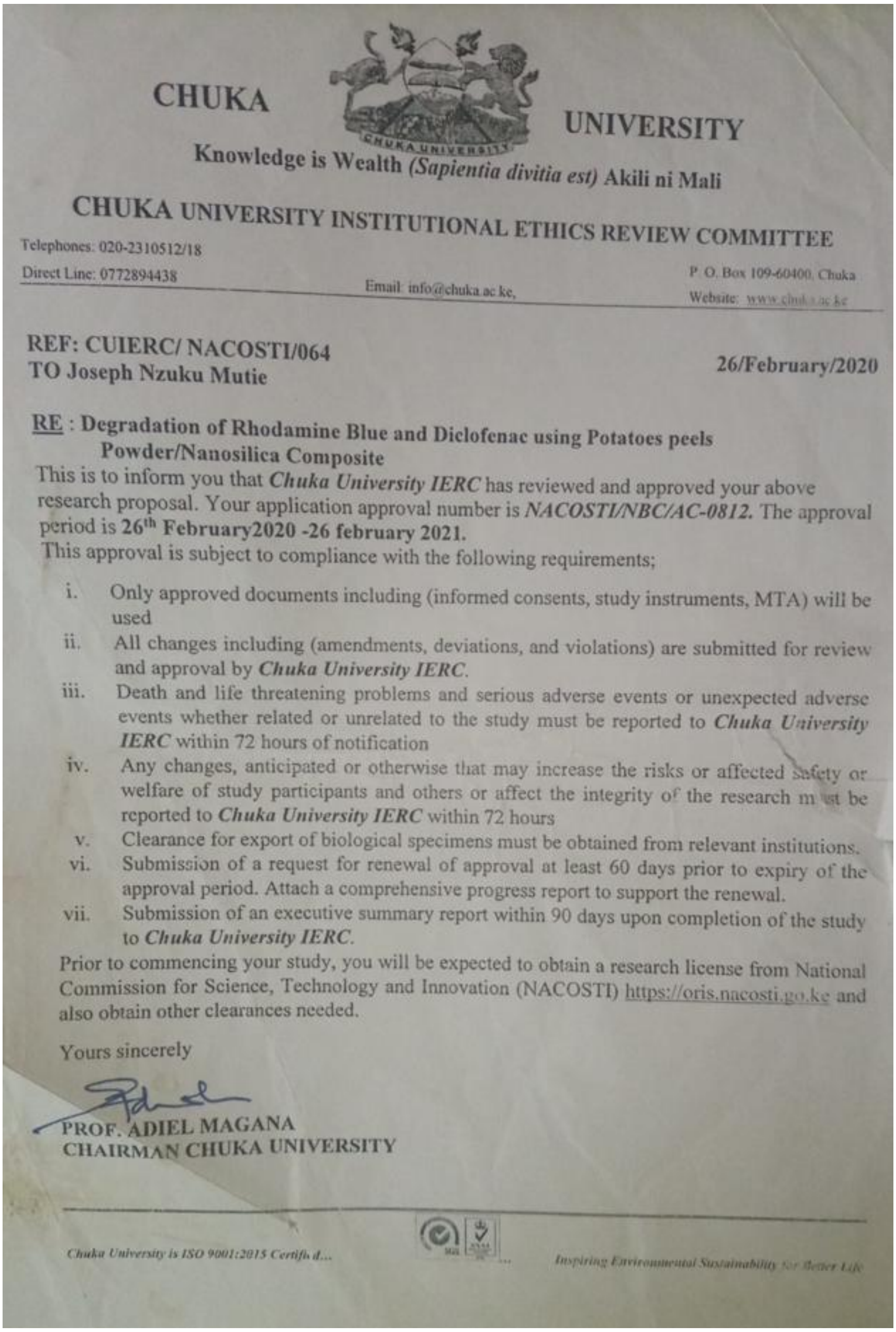
APPENDIX I: CALIBRATION CURVE OF DCF



Appendix II: Calibration Curve of RB



APPENDIX III: CHUKA UNIVERSITY IERC APPROVAL



CHUKA UNIVERSITY

Knowledge is Wealth *(Sapientia divitia est)* Akili ni Mali

CHUKA UNIVERSITY INSTITUTIONAL ETHICS REVIEW COMMITTEE

Telephones: 020-2310512/18
Direct Line: 0772894438
Email: info@chuka.ac.ke,
P. O. Box 109-60400, Chuka
Website: www.chuka.ac.ke

REF: CUIERC/ NACOSTI/064
TO Joseph Nzuku Mutie

26/February/2020

RE : Degradation of Rhodamine Blue and Diclofenac using Potatoes peels Powder/Nanosilica Composite

This is to inform you that *Chuka University IERC* has reviewed and approved your above research proposal. Your application approval number is ***NACOSTI/NBC/AC-0812.*** The approval period is **26th February2020 -26 february 2021.**

This approval is subject to compliance with the following requirements;

i. Only approved documents including (informed consents, study instruments, MTA) will be used
ii. All changes including (amendments, deviations, and violations) are submitted for review and approval by *Chuka University IERC*.
iii. Death and life threatening problems and serious adverse events or unexpected adverse events whether related or unrelated to the study must be reported to *Chuka University IERC* within 72 hours of notification
iv. Any changes, anticipated or otherwise that may increase the risks or affected safety or welfare of study participants and others or affect the integrity of the research must be reported to *Chuka University IERC* within 72 hours
v. Clearance for export of biological specimens must be obtained from relevant institutions.
vi. Submission of a request for renewal of approval at least 60 days prior to expiry of the approval period. Attach a comprehensive progress report to support the renewal.
vii. Submission of an executive summary report within 90 days upon completion of the study to *Chuka University IERC*.

Prior to commencing your study, you will be expected to obtain a research license from National Commission for Science, Technology and Innovation (NACOSTI) https://oris.nacosti.go.ke and also obtain other clearances needed.

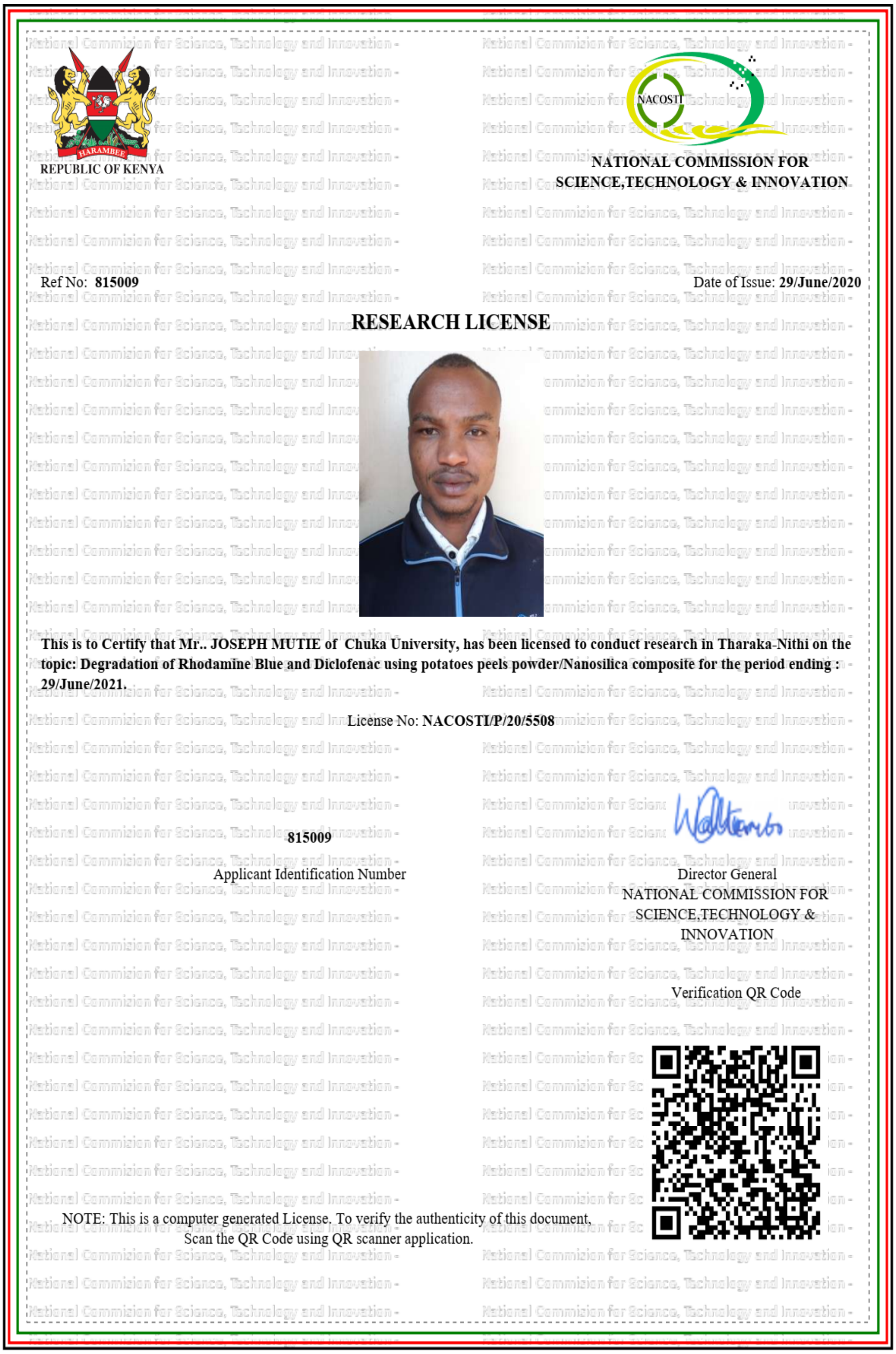
Yours sincerely

PROF. ADIEL MAGANA
CHAIRMAN CHUKA UNIVERSITY

Chuka University is ISO 9001:2015 Certified...

Inspiring Environmental Sustainability for Better Life

APPENDIX VI: NACOSTI RESEARCH LICENSE



REPUBLIC OF KENYA

NATIONAL COMMISSION FOR
SCIENCE,TECHNOLOGY & INNOVATION

Ref No: **815009**

Date of Issue: **29/June/2020**

RESEARCH LICENSE

This is to Certify that Mr.. JOSEPH MUTIE of Chuka University, has been licensed to conduct research in Tharaka-Nithi on the topic: Degradation of Rhodamine Blue and Diclofenac using potatoes peels powder/Nanosilica composite for the period ending : 29/June/2021.

License No: **NACOSTI/P/20/5508**

815009

Applicant Identification Number

Director General
NATIONAL COMMISSION FOR
SCIENCE,TECHNOLOGY &
INNOVATION

Verification QR Code

NOTE: This is a computer generated License. To verify the authenticity of this document,
Scan the QR Code using QR scanner application.