OXIDATIVE DEGRADATION OF TEXTILE WASTE WATER USING SNAIL SHELL AND FLOOR TILES AS AN ABSORBENT

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CERTIFICATION

This is to certify that this research project was carried out by AZAKA ABEL IGBUNUOGHENE of the department of chemical Engineering at the University of Benin, Benin city, Edo State, Nigeria.

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EXTERNAL EXAMINER	**DATE**

DEDICATION

I dedicate this project work firstly to God Almighty, and my lovely family and friends for their invaluable contributions and support throughout the course of my project work and also to everyone who has made this project a success.

ACKNOWLEDGEMENT

I want to start by expressing my sincere thankfulness to the All-Mighty God who has guided me so far, for His constant direction and blessings during this project and my time here at this bastion of learning. None of this would have been possible without His heavenly presence.

I owe a debt of appreciation to Professor F. A. Aisien, whose extraordinary leadership, insight, and mentoring have greatly influenced this research. His commitment to perfection has motivated me tremendously. Being able to work under his guidance has been extremely helpful, as his skills and mentorship have been essential. God Bless You Sir.

To my father and mother, your unending love, support, prayers and sacrifices have been my pillars of strength. Your sacrifices and belief in me have been instrumental in my success. God bless you.

To my brothers, the best brothers anyone could ask for. I owe a debt of gratitude for all your provisions, both materially and emotionally. Your encouragement and belief in my abilities and my potential have been a constant source of motivation. Heavens will reward you greatly

Lastly, I want to acknowledge two beautiful sisters for their unconditional love and support, which provided me with the emotional strength needed to persevere. To all my family, friends, students I have taught over the years and my well wishes, I say a big thanks to you all for the support and love.

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ABSTRACT

Textile wastewater poses a significant environmental threat due to its recalcitrant nature and toxic pollutants. This study explores the potential of snail shell and floor tiles as sustainable adsorbents for the oxidative degradation of textile wastewater. The adsorbents were characterized using FTIR,SEM,BET and XRF analyses. The effects of contact time, adsorbent dosage, and initial concentration on the degradation efficiency were investigated.

The Snail Shell And Floor tiles were purchased separately, processed and characterized to evaluate its suitability as an adsorbent. Batch adsorption studies were carried out by varying parameters such as adsorbent dosage, contact time, temperature ,pH and initial dye concentration. The adsorption mechanism was predicted by some kinetic models such as pseudo-first-order, pseudo-second-order, intra particle diffusion model and Elovich model.

The results of batch adsorption study showed that for unactivated and activated snail shell and floor tiles increasing the adsorbent dosage and contact time resulted in increased percentage dye removal while increasing the pH and initial dye concentration resulted in decrease in percentage dye removal. The optimum conditions for maximum percentage dye removal for unmodified and modified bio adsorbent are 2.5g adsorbent dosage, 75minutes contact time, and 25mg/l initial dye concentration. The best percentage dye removal were 268.59 % and 251.61% using unactivated and activated bio adsorbent. The sorption kinetics for the adsorption processes were found to be best represented by the pseudo-second-order kinetic equation, as its R2 values were greater than 0.98. and the qe experimental and qe calculated are virtually equal. The Elovich model also showed a significant fitting to the kinetics of the adsorption process as its R2 values were also high. This suggests that chemisorption with heterogeneous sorption mechanism is likely responsible for congo red dye uptake.

CHAPTER ONE

INTRODUCTION

1.0 Background of the study

Anthropogenic activities, especially from the manufacturing textile industrial sectors, are a significant source of water pollution due to their non-biodegradable chemical structure and their persistence in the environment (Baloo, *et al., 2021)*. The textile industry generates more than 700 tonnes of dyes annually, of which 50% is released into the receiving water (Islam, *et al., 2017)*.

Due to the associated risks and hazardous effects of dye effluents on the environment and within the receiving water, the negative impact on the exposed population, both humans and the aquatic microorganism is of utmost concern (Misran, *et al*.,2022) From the global perspective, the utilization of synthetic dyes by industries such as textile and painting is on a geometric increase.

Several million tonnes of dyes are consumed in the production phase of materials as a colouring agent (Tsamio, *e al.,*2023). Due to its physical, chemical, and thermal stability, Congo red (CR) is typically a widely consumed anionic diazo dye. The stability of the chemical structure of CR dye can be attributed to its aromatic rings and azoic linkages. CR dye is non-biodegradable due to its stable structure; as a result, it causes severe health disorders in humans. Despite its wide application, several reports describe its hazardous effects (Nizam, *et al*., 2022).

Furthermore, the presence of a residual concentration of the dye, even at low concentrations when it is discharged into the receiving water, can compromise the aesthetic quality of surface water; its bioaccumulation can cause toxicity and carcinogenicity and can also impact the health of humans and the environment (Elamin *et al.,* 2023). Hence, removing CR is a significant research topic.

So far, adsorption is a suitable decontamination technique and has been applied widely for pollutant remediation and water purification, attributed to its treatment efficiency at a relatively low operational cost (Postai, *et al., 2016)*. Therefore, adsorbents with enhanced efficiency for pollutant removal from wastewater streams are being processed to achieve cost-effective products as suitable materials for dye removal. Many researchers have utilized alternative

materials to serve these purposes. Activated carbon from low-cost biomass or waste materials has extensively been investigated for dye adsorption (Aftab, *et al*., 2023).

The synthesis of bio-waste precursors as carbonaceous materials has always fallen in the category of a sustainable approach towards its utilization for dye removal due to its large surface area for binding pollutants (Oyekanmi, *et al., 2021).* Recently, nanomaterials for the removal of dyes have gained considerable attention. Nanoparticles have remarkable prospects for greater adsorption efficiency due to their intrinsic surface area and active pores, including their non-

toxicity (Rashtbari, *et al., 2022)*. Plant extracts have been extensively exploited for synthesizing green nano biomaterials due to their abundance and renewability potential (Reshmy, *et al.,* 2022) However, the utilization of biogenic wastes as a nanoparticle source appears promising due to their abundance, potential for material renewability, and biodegradability.

Snail shell, composed of calcium carbonate, are a typical natural biomineralized shell and can be used for material synthesis and pollution remediation (Lu, *et al., 2021)*. Research has been carried out on many economic minerals, other than for dye adsorption, calcium carbonate-derived nanoparticles were only investigated for fluoride adsorption from an aqueous solution (Brinza, *et al., 2022)*. Snails belong to the class *Rostellaria* and this type of snail is found frequently at the edges of the beaches and lakes. The snail shell has the same basic construction as other Mollusk shells. It consists of three layers. The Periostracum, the outermost shell layer, is not made of CaCO3, but of an organic material called Conchin, a mixture of organic compounds, mostly of proteids. Conchin not only makes the outer shell layer, but also embedded between the CaCO3 crystals of deeper layers (Hassanine, *et al.,* 2010). Thus, this research offers low cost and readily available adsorbents that could be employed in the treatment of wastewater and the optimal conditions for maximum sorption efficiency.

1.1 Aim and objectives

This study aims to examine the adsorption of congo red dye using snail shell and floor tiles as bio adsorbent.

1. To investigate the effectiveness of snail shell and floor tiles as a bioadsorbent for the removal of Congo Red dye from aqueous solutions.
2. Conduct batch adsorption experiments to study the adsorption equilibrium and determine optimal conditions.
3. Evaluate the effect of adsorbent dosage, contact time, initial dye concentration, pH, and temperature on the adsorption process and compare the percentage dye removal of unactivated and activated snail shell and floor tiles on varying these parameters
4. Investigate the kinetic and isothermal behavior of Congo Red dye adsorption onto snail shell and floor tiles bio adsorbent

1.2 Scope of Study

The scope of the study can cover several aspects. these includes;

1. Characterization of the bio adsorbent**:** This involves XRD, XRF, FTIR, SEM and BET analysis. Analyzing its structural, chemical, and physical characteristics helps in determining factors like surface area, porosity and composition can help understand its adsorption capabilities.
2. Adsorption studies: The project can explore the optimization of various parameters that influence the adsorption process, such as pH, temperature, initial dye concentration, adsorbent dosage, and contact time. This will help determine the optimal conditions for maximum adsorption efficiency.
3. Adsorption kinetics**:** The project can look at the kinetics of adsorption of Congo red dye onto tiger nuts. This includes studying the behavior of the pace at which adsorption takes place. The experimental data can be analyzed using a number of models, including pseudo-first-order, pseudo-second-order kinetics, Elovich model and Intra-particle diffusion model
4. Thermodynamic study**:** Determination of the thermodynamic parameters (Enthalpy, Entropy and Gibbs free energy) by varying the temperatures. This analysis provides insights into the spontaneity and feasibility of the adsorption process.

1.3 Problem Statement

The presence of synthetic dyes, such as Congo Red, in industrial effluents poses a significant environmental challenge due to their toxicity and potential harm to aquatic ecosystems. Traditional methods of dye removal are often costly and unsustainable. Thus, there is an urgent need to develop an eco-friendly, cost-effective, and efficient approach for removing Congo Red dye from wastewater. This project aims to address this issue by investigating the potential of snail shells as a natural and renewable biosorbent for adsorbing Congo Red dye. The study will focus on determining the percentage of dye removal and exploring factors that influence the adsorption process, including adsorbent dosage, contact time, pH, temperature, and initial dye

concentration. Additionally, the project will investigate the kinetics of Congo Red dye adsorption onto snail shells.

1.4 Relevance of the study

1. Environmental impact**:** A serious environmental risk is posed by the poisonous and persistent congo red dye. The use of snail shell as a bio adsorbent for Congo red dye removal can help reduce this threat by offering an environmentally friendly and long-lasting alternative.
2. Low-cost adsorbent: Snail shell is a common and inexpensive agricultural waste product that can be used as a bio adsorbent. This makes it a desirable substitute for expensive commercial adsorbents**.**
3. Optimization of adsorption conditions: The study can investigate how to best control a number of variables, including pH, temperature, starting dye concentration, adsorbent dosage, and contact time.
4. With the aid of this optimization, the optimal conditions for achieving the greatest adsorption efficiency will be determined. This can be useful for future research and applications.

CHAPTER TWO

LITERATURE REVIEW

2.1 Oxidative degradation

Research on oxidative degradation of dye molecules is crucial due to environmental concerns. Azo dyes, widely used in various sectors, cause pollution, oxygen consumption, and harm to aquatic life due to their persistence and resistance to decomposition. Oxidative degradation is the process of macromolecules disintegrating due to oxygen action, resulting in the formation of free radicals and hydrogen removal, and can be initiated by UV light, heat, or mechanical stress. (Iannuzzi, Mattsson, and Rigdahl, 2013).

Oxidative degradation is also the method used to break down organic compounds, such as Congo red dye, which poses health and environmental risks due to its resistance to breakdown due to its aromatic structures in its chemical makeup. This process can help reduce Congo red dye to simpler compounds.

2.2 Dyes

Dyes are colored substances that chemically bond to substrates, differing from pigments. They are typically applied in aqueous solutions and may require a mordant for better adhesion. (Booth, Gerald (2000))

According to Britannica, "Dye, a substance used to impart color to textiles, paper, leather, and other materials such that the coloring is not readily altered by washing, heat, light, or other factors to which the material is likely to be exposed. They chemically bond to the substrate to which it is being applied ensuring the color remains intact.

Dye is an extremely important component in the textile industry as it is used to color fabrics. The dyeing process takes place at various points during the production of textiles, including when creating fiber, yarn, fabric, or finished textiles. The textile industry uses a variety of colors, including both synthetic and natural dyes. While synthetic dyes are created artificially and developed in a laboratory, natural dyes are created by extracting natural pigments from plants, animals, and minerals.

2.2.1 Types of Dye

(Dipa Aryal 2022) Very common classification of the dyestuff is based on the source from which it is made. Accordingly, the classification could be:

1. Natural Dyes
2. Synthetic Dyes

NATURAL DYES

Natural dyes are dyes obtained from natural sources like plants, invertebrates, or minerals. Vegetable colors made from plant materials make up the majority of all natural dyes. For instance, roots, berries, bark, leaves, and wood, while fungi and lichens are among the other organic sources

- Synthetic Dye

Today, synthetic dyes are used to produce almost all of the colors. Synthetic dyes are employed everywhere, from clothing to paper, from food to wood, this is due to the fact that they are easier to apply to fabrics, brighter, more color-fast, and less expensive to manufacture. Examples: Acid dyes, Azo dyes, Basic dyes, Mordant dyes, etc.

- Azo Dyes

The majority of synthetic dyes contain nitrogen as the azo group -N=N- as a primary chromophore, and these dyes are known as azo dyes. The food, pharmaceutical, cosmetic, textile, and leather sectors all utilize these dyes extensively. These dyes are produced by diazotizing an aromatic amine and combining it with an appropriate aromatic molecule. They are highly colorful dyes. One or more aromatic azo groups serve as the chromophoric component in this class of dyes.

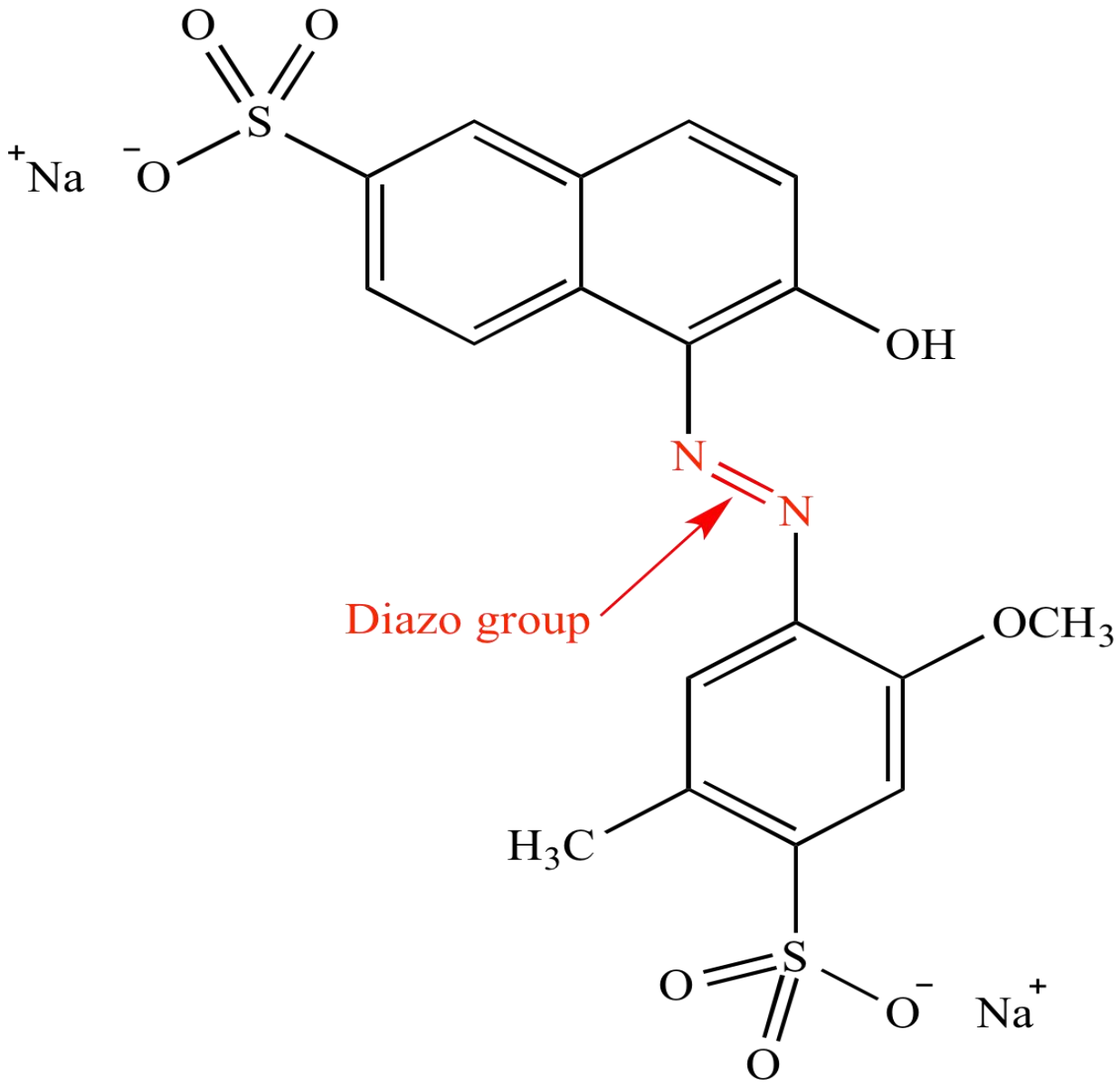
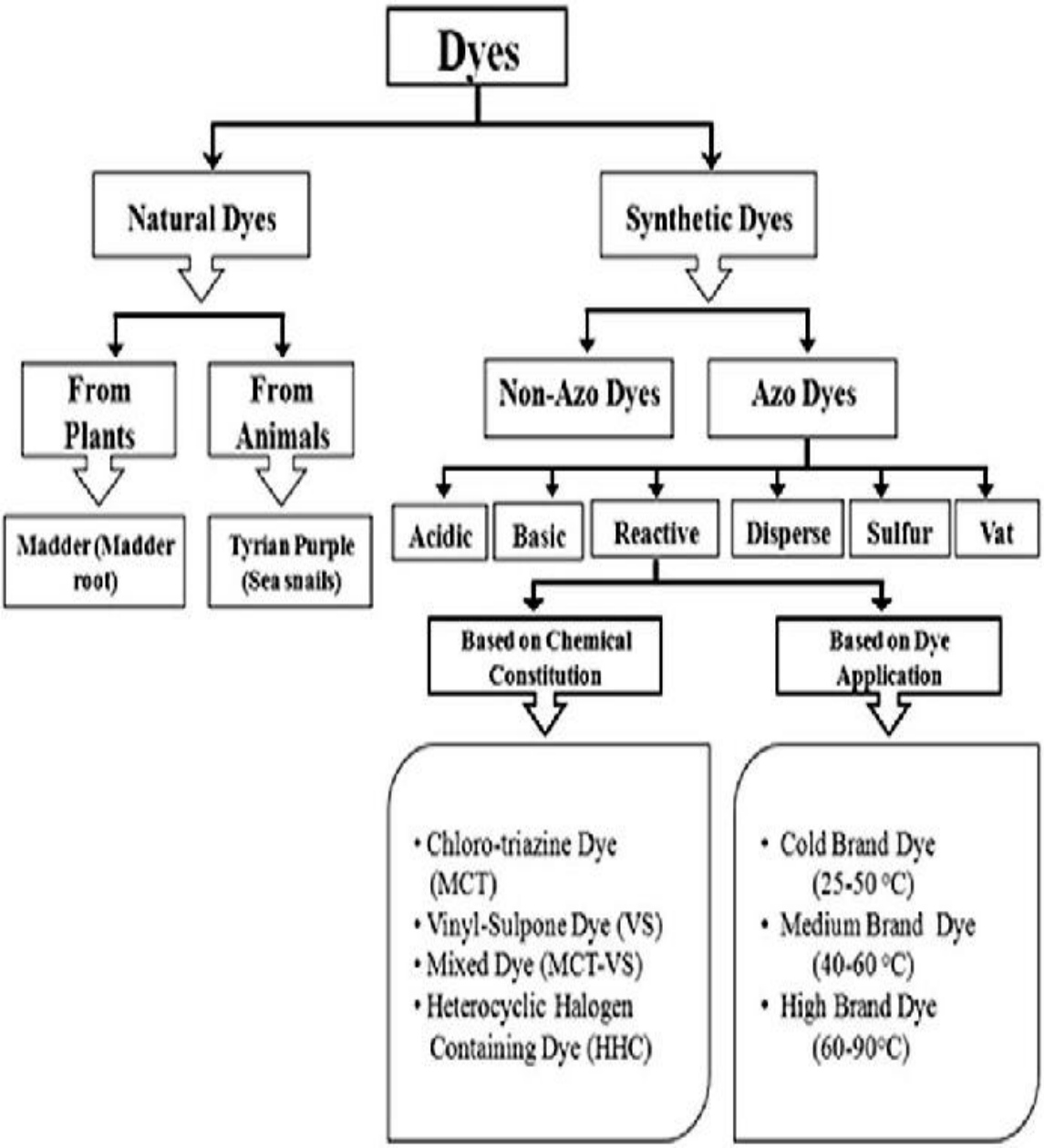


Figure 2.1: Diagram of Azo Dye

2.2.2 Classifications of Dyes



2.2.2.1 Based on application

1. Vat dyes: Suited for cellulose fiber fabrics, these dyes offer excellent light and water washing fastness, as well as resistance to chlorine bleaching and other oxidative bleaching agents.
2. Reactive dyes: Mostly used on cellulose fiber fabrics and less commonly on protein fibers. They are known for their bright colors, good light fastness, and excellent water washing and rubbing fastness.
3. Direct dyes: Ideal for cellulose fiber fabrics. They have relatively poor color fastness to water washing and varying light fastness. However, modified direct dyes can significantly improve their color fastness to water washing.

2.2.2.2 Based on their ionic nature

1. Acid dyes: Primarily suitable for protein fibers, nylon, and silk, among others. They are known for their vibrant colors but have poor color fastness to water washing. However, they exhibit excellent dry-cleaning fastness and are widely used in natural dyeing.
2. Cationic dyes (Basic dyes): Suited for acrylic, polyester, nylon, cellulose, and protein fibers. These dyes offer bright colors and are well-suited for synthetic fibers. However, they have poor color fastness to water washing and light, especially when used on natural cellulose and protein fabrics.
3. Disperse dyes: Suitable for viscose, acrylic, nylon, polyester, and similar fibers. They exhibit varying color fastness to water washing, with better results on polyester and poorer results on viscose.

2.2.2.3 Based on chromophoric groups

1. Azo dyes (Naphthol dyes): Suitable for cellulose fabrics, offering bright and vibrant colors.
2. Sulfur dyes: Suitable for cellulose fiber fabrics, these dyes provide dull and dark shades such as navy blue, black, and brown. They exhibit excellent light and water washing fastness but poor chlorine bleaching fastness. Prolonged storage of fabrics dyed with sulfur dyes can cause fiber damage.

3. Nitro dyes: Nitro dyes contain at least one nitro group in the aromatic ring, either ortho or para to an electron-donating group (often hydroxyl, imino, or amino groups).

4. Triarylmethane dyes**:** Paper, leather, plastic, and inks for writing, printing, and stamping are all colored with triarylmethane dyes. Triarylmethane dyes are used to color polyacrylonitrile fibers.

2.3 CONGO RED

Congo Red is a chemical substance, more precisely the sodium salt of 3,3′-bis(4-dimethylaminophenyl) azobenzene-4′-sulfonic acid. It belongs to the azo dye family and differentiates itself by its bright red color. Congo Red is water-soluble and can form a red colloidal solution, with greater solubility in organic solvents. Its chemical formula is $C_{32}H_{22}N_6Na_2O_6S_2$, and it has a molar mass of approximately 696.665 grams per mole.

2.3.1 Brief History of Congo Red

Congo red was first synthesized in 1883 by Paul Böttiger, who had been employed at Friedrich Bayer Company in Elberfeld, Germany. He was looking for textile dyes that did not require a mordant step.

The company which had a right of first refusal to his inventions was not interested in this bright red color, so he filed the patent under his own name and sold it to the AGFA company of Berlin. AGFA marketed the dye under the name "Congo red", a catchy name in Germany at the time of the 1884 Berlin West Africa Conference, an important event in the Colonization of Africa. The dye was a major commercial success for AGFA. In the following years, for the same reason, other dyes were marketed using the "Congo" name: Congo rubine, Congo corinth, brilliant Congo,

Congo orange, Congo brown, and Congo blue. Once of economic significance, Congo red has fallen into disuse as have all benzidine-derived dyes, owing to their carcinogenic activity (Steensma, 2001) Congo Red has various applications, including its use as a textile dye and in biological staining techniques.

Additionally, it is employed in research to investigate its interactions with different substances and its toxicity.

Table 2.1: Characteristics of Congo red dye

Other Names (IUPAC)	disodium;4-amino-3-[[4-[4-[(1-amino-4-sulfonatonaphthalen-2-yl) diazenyl]phenyl]phenyl]diazenyl]naphthalene-1-sulfonate
Type	A synthetic anionic diazo dye. dissolves and releases an anion of the sulfonate group (CR-SO3) in the aqueous solution.
Chemical formula	$C_{32}H_{22}N_6Na_2O_6S_2$
Molecular Weight	696.66 g/mol
Purity	99.99%
Maximum Wavelength (nm)	497
C.I. NO:	22120
CAS NO:	573-58-0

2.4 DYES IN THE ENVIRONMENT

Significant amounts of dye are released into the environment during dye production and consumption, which has a higher impact on water quality. These dyes affect the amount of light reaching the water when they are injected, which has an effect on aquatic life. Since a little amount of synthetic dyes in water may be seen, this affects the aesthetic value, transparency, and gas solubility of water bodies. Additionally, color is often a clearly recognizable pollutant in wastewater. They hinder photosynthesis and obstruct the development of aquatic organisms by reflecting and absorbing sunlight that enters the water. According to the concentration and length of exposure, they can potentially have acute or chronic effects on organisms.

Despite the fact that totally reducing toxicity is also required, the main objective is to decolorize wastewater that contains dyes. The regulations governing the removal of dyes from industrial effluents are becoming strict in both industrialized and developing countries. The law will continue to be upheld to ensure that industries using dyes in textiles and other industries treat their effluent to the required standards.(Zafar S. Et al.,2022)

2.4.1 Technology used to treat effluents that contain dye

Wastewater that contains dyes can be challenging to treat since the organic chemicals are meant to be resistant to light and aerobic digestion (Valli Nachiyar et al., 2023)

The three different types of dye removal methods are biological, chemical, and physical.

1. **Physical method**

Owing to the absence of live organisms and chemicals, this approach is said to be more trustworthy than the other two dye removal techniques. Membrane filtration and adsorption procedures are two common physical approaches. With the adsorption approach coming in top rank, the greatest removal percentage for physical dye removal procedures is between 86.8% and 99%.

2. **Chemical methods**

Chemical Treatment: Chemical techniques involve the use of chemicals like coagulants and flocculants to precipitate and remove dyes. This process is relatively quick but may generate chemical sludge. Chemical dye removal methods have a number of shortcomings that render them unsuitable for commercial application, including the necessity for equipment, high electrical energy requirements for reactors, and substantial chemical reagent consumption.

3. **Biological Treatment method**

Biological methods utilize microorganisms to break down dye molecules. The use of biological treatment is both economical and advantageous to the environment. The two basic phases in the treatment of dyes are the first step, where the azo linkages are broken under anaerobic conditions to produce the amines, and the second step, where the aromatic amines are further broken down under aerobic conditions into minute harmless molecules.

Because biological treatment interferes with bonds in the chromophoric group to help with dye removal, it is less hazardous than chemical treatment but may require longer treatment times.

2.4.2 USES OF DYE

1. **Textile dyeing:** In the textile industry, dyes are frequently used to tint fabrics made from a variety of fibers, including cotton, wool, silk, and synthetic fibers like polyester, nylon, and acrylic. Cotton, paper, leather, wool, silk, and nylon are all dyed using direct dyes whilst polyester is primarily dyed using disperse dyes
2. **Applications in medicine**: Dyes are employed as biological stains and pH indicators. In the manufacturing of some lasers, optical media (CD-R), and camera sensors (color filter array), laser dyes are employed.

2.5 OVERVIEW OF SNAIL SHELL

The snail shell is one of the most astonishing wonders of evolution in all of the animal kingdom. The name snail though applies to all gastropods; it commonly means only those species with an external shell large enough that the soft part can withdraw into.

Those gastropods without a shell, and those with only small or reduced inner shells are known as slugs (Bouchet and Rocroi, 2005). This hard and fleshless shell protects the visceral hump, that is, the soft and flexible body which is absent from the skeleton both internal and external. The shell is not however permanently attached to the body of the snail. The snail belongs to the phylum Mollusk and class gastropods. The gastropods are the largest class of the phylum Mollusk (Brunt et al., 1999), a group of animals commonly known as snails and slugs.

Land snails live among wet vegetation in damp and shady places, they are more abundant in rainy seasons and most active at night. There are also snails that live in sea which are known as sea snails and those that live in freshwater known as fresh water snails (Brusca and Brusca, 2003). The snail's soft body consists of a head, a foot, and a visceral mass or lump, which remains permanently inside a hard protective shell (Poppe and Tagaro, 2006). Gastropods have worldwide distributions from near Arctic and Antarctic zones to the tropics.

They are found predominately in West Africa, all gastropods at some time in their phylogeny and at some stage in their development have undergone an anatomical process known as torsion. The process does not occur in any other mollusk and this distinguishes snails from other mollusks. It implies that the visceral mass and the mantle shell covering it have become twisted through 180^0 in relation to the head and foot. As a result of torsion, all internal organs are twisted into a loop (Aboua, 1995). More than half of all mollusk species are gastropods and encompass a range from marine, zygo branch, which can be numbered among the most primitive of all living mollusks, to the highly evolved terrestrial air breathing slugs and snails.

The shell of the large land snail is brownish yellow in colour with dark markings and is up to 10 cm or more in length, it is very hard. Snail shell has several important uses, which results from the hard nature of the shell. The shell protects the snail from physical damage, predators and dehydration. They are used also in the manufacture of buttons, jewels, and art collection. Recent development involves its application in the treatment of water and wastewater resulting from its chemical composition and large surface area; this composition includes proteins, carbohydrates, fats, and minerals such as iron, zinc, copper, etc. (Botkin and Edward, 1988).

Diagram of Snail shell

Figure 2.2: Diagram of a Dry Snail shell

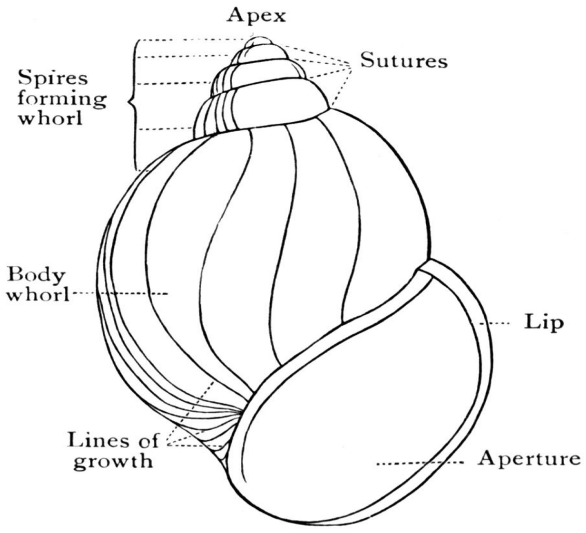


Plate 1: fresh Snail shell

Snail shell Products

1. Snail Shell Powder: Snail shell powder is a versatile product derived from finely ground snail shells. The powder is primarily composed of calcium carbonate, with traces of other minerals and proteins. It finds applications in agriculture, cosmetics, and pharmaceuticals due to its rich mineral content and potential benefits for soil improvement, skin care, and wound healing (Baloyi, 2019).
2. Snail Shell Calcium Supplements: Calcium supplements sourced from snail shells offer a natural alternative to traditional calcium sources. These supplements are rich in calcium carbonate, which is easily absorbed by the body. Studies suggest that calcium derived from snail shells may have comparable efficacy to calcium carbonate from other sources in improving bone mineral density and preventing osteoporosis (Cruz-Jentoft et al., 2020).
3. Snail Shell Cosmetics: The cosmetic industry has embraced snail shell extracts for their purported benefits in skincare. Snail mucin, extracted from snail shells, contains glycoproteins, hyaluronic acid, and antioxidants that moisturize the skin, reduce inflammation, and promote collagen production. Snail shell extracts are commonly found in serums, creams, and masks, touted for their anti-aging and skin-repairing properties (Tsoutsos et al., 2016).

4. Snail Shell Fertilizers**:** Snail shell-based fertilizers are gaining popularity in sustainable agriculture practices. The calcium-rich composition of snail shells improves soil structure,

regulates pH levels, and enhances nutrient uptake by plants. Additionally, the slow decomposition of snail shells releases nutrients gradually, providing long-term benefits to soil health and crop productivity (Odu et al., 2021).

5. Snail Shell Crafts: Artisans and hobbyists utilize snail shells in various craft projects due to their unique shapes and patterns. Snail shells can be cleaned, polished, and decorated to create jewelry, ornaments, and decorative pieces. These crafts not only showcase the natural beauty of snail shells but also promote creativity and environmental awareness by repurposing organic materials (Eguakun et al., 2018).

2.5.2 Nutritional Benefits of Snail shell

1 **Calcium Source:** Snail shells are rich in calcium carbonate, comprising about 95% of their shell composition. Calcium is an essential mineral for bone health, muscle function, and nerve transmission (Liu & Sheng, 2020). Incorporating snail shell powder or extracts into the diet can contribute to meeting daily calcium requirements, especially for individuals at risk of calcium deficiency or osteoporosis.

2 **Mineral Supplement:** Apart from calcium, snail shells contain traces of other minerals such as magnesium, potassium, and phosphorus. These minerals play vital roles in various physiological functions, including energy metabolism, muscle contraction, and electrolyte balance (Tsoutsos et al., 2016). Incorporating snail shell-derived supplements into the diet can help maintain mineral balance and support overall health.

3 **Alkalizing Effect:** Snail shells have an alkalizing effect on the body due to their calcium carbonate content. Alkaline diets are believed to counteract the acidic effects of modern diets high in processed foods and animal proteins, potentially reducing the risk of chronic diseases such as osteoporosis, hypertension, and kidney stones (Schwalfenberg, 2012).

Consuming snail shell products may contribute to maintaining a healthy pH balance in the body.

4 **Digestive Aid:** The abrasive texture of snail shell powder may act as a mild digestive aid. When ingested, the fine particles of snail shells can help to mechanically break down food particles in the gastrointestinal tract, facilitating digestion and nutrient absorption (Baloyi, 2019). This property makes snail shell powder a potential ingredient in digestive health supplements and remedies.

5 **Natural Antacid:** Calcium carbonate, the primary component of snail shells, is commonly used as an antacid to relieve symptoms of acid reflux and indigestion. By neutralizing excess stomach acid, calcium carbonate can alleviate heartburn and promote gastric comfort (Dhakal et al., 2021). Incorporating snail shell-derived calcium supplements or antacids into the diet may offer natural relief for digestive discomfort.

2.5.3 Chemical Compositions of Snail shell

Snail shells, the protective coverings of gastropod mollusks, exhibit a complex chemical composition that confers structural integrity and resilience. Analyzing the chemical constituents of snail shells reveals a diverse array of minerals and organic compounds essential for both the mollusk's physiology and potential applications in various industries. The chemical composition results in snail shells per 100 grams.

1. **Calcium Carbonate (CaCO3):** Predominantly, snail shells consist of calcium carbonate, comprising approximately 95% of their composition (Baloyi, 2019).
2. This mineral provides the structural framework of the shell, imparting strength and rigidity. Calcium carbonate also serves as a valuable source of dietary calcium for humans, contributing to bone health and mineral balance.
3. **Protein:** Snail shells contain a modest amount of protein, typically ranging from 30% to 40% of their dry weight (Chen et al., 2016). These proteins play essential roles in shell formation, contributing to the organic matrix that facilitates mineral deposition and shell growth.

Additionally, snail shell proteins may exhibit bioactive properties with potential applications in biomedical research and materials science.

4. **Magnesium (Mg):** Magnesium is present in snail shells in trace amounts, usually less than 1% of the shell's composition (Hou et al., 2020). Despite its relatively low concentration, magnesium plays crucial roles in biomineralization processes, influencing crystal morphology and structure. The presence of magnesium ions in snail shells may contribute to their mechanical properties and resistance to environmental stressors.
5. **Phosphorus (P):** Phosphorus is an essential component of the organic matrix within snail shells, contributing to approximately 1% of the shell's composition (Tsoutsos et al., 2016). Phosphorus compounds participate in shell formation by regulating mineralization processes and influencing crystal nucleation and growth. The presence of phosphorus in snail shells underscores its importance in maintaining shell integrity and functionality.
6. **Other Minerals:** In addition to calcium, magnesium, and phosphorus, snail shells may contain trace amounts of other minerals such as potassium, sodium, and iron (Baloyi, 2019). These minerals contribute to the overall nutritional profile of snail shells and may have implications for human health and agricultural applications.

Understanding the chemical composition of snail shells provides valuable insights into their structural properties, nutritional value, and potential industrial applications. From serving as a sustainable source of calcium and protein to offering inspiration for biomimetic materials, snail shells represent a multifaceted natural resource worthy of further exploration and utilization.

2.5.4 Usage of Snail shell

The shell of a snail, known as a "snail shell" or "gastropod shell," serves various purposes beyond simply providing protection for the snail's body.

Snail shells are utilized in various forms of art and craftwork, including jewelry making, sculpture, and decorative items. The intricate patterns and unique shapes of snail shells make them popular among artists and artisans.

Crushed snail shells are often used as a source of calcium in agriculture, especially in regions with calcium-deficient soils. The calcium content in snail shells can help improve soil fertility and enhance plant growth.

Traditional medicine systems in various cultures have utilized powdered snail shells for medicinal purposes, including treating stomach ailments and promoting bone health. The calcium carbonate present in snail shells is believed to have therapeutic properties.

Snail shells, both natural and artificial, are commonly used as decorative elements in aquariums. They provide shelter for small aquatic creatures, contribute to the naturalistic environment, and serve as substrate for algae growth.

Snail shells are valuable educational tools in biology classrooms and research laboratories. They are used to study mollusk anatomy, evolutionary biology, shell formation, and ecological interactions.

2.6 ADSORPTION MECHANISM

Adsorption is the process where molecules or ions from a liquid or gas adhere to the surface of a solid material. Adsorption offers great potential for effectively eliminating dyes from various sources. This approach is known for its efficiency, adaptability, simplicity in design, eco-friendliness, cost-effectiveness, and widespread application in the field of color removal (Kani et al., 2020).

Adsorption is the phenomena of attraction and retention of the molecules of a liquid "adsorbate" by a solid "adsorbent" on its surface, which results in an increased number of molecules on the surface. Three stages make up the standard adsorption mechanism: Adsorbate surface diffusion: by the adsorbate's migration through the adsorbent's pores, the adsorbate's formation of monolayers on the adsorbent, and the intermolecular forces between the adsorbent and the adsorbate: Particles of adsorbate from the monolayer of molecules, ions, and atoms that reacted with the active sites of the absorbent are dispersed throughout the surface and fill the space of the pores (Benjelloun et al., 2021).

Adsorption is a crucial process in which substances are transferred from fluids like gases or liquids to a solid surface, often used for removing pollutants. This process occurs naturally in various environmental settings and involves the adhesion of solute molecules or ions to a porous solid surface. It's a form of mass transfer that takes advantage of the distinct surfaces between liquids and solids or even between solid materials. (Zhou, 2006). Dye molecules may be drawn to and aggregated on the surface of the adsorbent during the adsorption process by a variety of forces, including hydrogen bonds, electrostatic interactions, van der Waals forces, and hydrophobic interactions. The shape, size, radius, polarity, presence of effective groups, molecular weight, solubility, surface area, hydrogen ion concentration (pH) of the solution, temperature, mixed solutes, and nature of the adsorbate all have an impact on the interaction between the adsorbent surface and the adsorbed particles (Mahmood Aljamali et al., 2021).

2.6.1 TYPES OF ADSORPTION

1. Physical Adsorption

In Physical Adsorption, because of the bonds formed between atoms and neighboring atoms of the same substance, adsorption occurs on these surfaces through natural attractive forces known as van der Waals forces. This type of adsorption can manifest as multiple layers of the adsorbent material accumulating on the surface of the adsorbent material under suitable conditions of pressure and temperature. Importantly, the interaction between the adsorbent and the adsorbate, estimated to be less than 40 kJ/mol, allows this process to take place at relatively low temperatures, similar to the condensation of vapors on the surfaces of liquid materials(Mahmood Aljamali et al., 2021).

2. Chemical Adsorption

The chemisorption process, which forms chemical bonds with the adsorbed atoms or molecules, takes place on surfaces that are not electrically unsaturated. Chemisorption needs a higher activation energy than physisorption, frequently needing high temperatures above 40 kJ/mol. It is a unique, irreversible process that is frequently constrained by the development of a monolayer on the adsorbent surface. Examples include hydrogen chloride chemisorption on iron surfaces and oxygen chemisorption on coal surfaces.

Chemisorption processes are influenced by a number of variables, including temperature, pressure, and the makeup of the adsorbent and adsorbate.(Mahmood Aljamali et al., 2021).

2.6.2 Differences Between Physisorption and Chemisorption

Table 2.2: Difference between physical and chemical adsorption

S/N	PHYSISORPTION	CHEMISORPTION
1.	Physisorption occurs due to Van Der Waals forces.	Chemisorption occurs due to the creation of chemical bonds
2.	Physisorption is reversible in nature	Chemisorption is irreversible in nature
3.	Physisorption is non-specific.	Chemisorption is relatively specific in nature.
4.	The activation energy is low.	The activation energy is quite high.
5.	Multi layers or Monolayers	Monolayers
6.	A rise in temperature results in a reduction in the physisorption process.	As temperature rises, the chemisorption process accelerates.
7.	It is independent of the nature of the adsorbent.	It is independent on the nature of the adsorbent

2.6.3 Factors Affecting Adsorption

2.6.4 Effect of pH

In dye adsorption procedures, the pH of the adsorptive solution is an important consideration. It has significant effects on how dye molecules interact with the adsorbent surface in aqueous solutions. pH has an influence on the chemistry of both the dye and the adsorbent. The adsorption of various colors has been the subject of much research on these phenomena.

The ionization state of the dye molecules can be affected by the pH of the solution. Their affinity for the adsorbent surface is thus affected by this. Depending on the pH, charged groups on dye molecules may be protonated or deprotonated, changing how electrostatically the dye interacts with the adsorbent. Additionally, the pH of the adsorbent itself can alter its surface charge, which affects how it interacts with dye molecules (de Farias et al., 2018)

2.6.4.1 Effect of Contact Time

In the adsorption process, contact time is crucial. It has an impact on the adsorption kinetics, which controls how rapidly compounds are adsorbed onto surfaces, as well as on the economy. In practical applications, maximizing contact duration can improve the effectiveness of adsorption processes, assuring the highest removal of target compounds while reducing resource consumption. The effect of contact time on adsorption efficiency is investigated in a number of studies in the field of adsorption, including those involving graphene sand composites, heavy metal removal, and Langmuir adsorption kinetics.

These studies offer insights into how to modify adsorption processes for particular applications. Designing efficient adsorption systems therefore requires an understanding of and control of contact time (Hammari et al., 2021)

2.6.4.2 Effect of Adsorbent Dosages

Adsorbent dosage, or the amount of adsorbent utilized, is an important variable for estimating the adsorption capacity in particular operating instances. Usually, a higher adsorbent dosage results in increased removal efficiency. This happens because additional adsorbent provides more sorption sites on its surface, enabling the adsorption of more of the target chemical, like dyes. Adsorbent dose impact is a crucial factor in adsorption process optimization. It provides useful information on the connection between the quantity of adsorbent used and the level of adsorption attained. It is possible to evaluate the economic viability of an adsorption process by comprehending this relationship. It assists with figuring out how well a dye or other substance may be removed with the least amount of adsorbent material, which is important for affordable and environmentally friendly adsorption methods (Ma et al., 2014).

2.6.3.4 Effect of Temperature

Temperature is an important physico-chemical variable that significantly impacts the adsorption process. Depending on temperature changes, adsorption can act in both an exothermic and an endothermic manner

- Endothermic Adsorption**:** An endothermic process is one in which the temperature rises as well as the rate of adsorption. In such cases, the increased temperature increases the number of active adsorption sites on the surface of the adsorbent and improves the mobility of dye molecules. This results in an increase in adsorption capacity.
- Exothermic Adsorption: On the other hand, an exothermic reaction is present if the adsorption capacity falls as the temperature increases. When this happens, the adsorption process produces heat, which causes the adsorption capacity to decrease at higher temperatures.

2.6.4.3 Effect of Dye Concentration

The concentration of the initial dye solution plays a pivotal role in determining the quantity of adsorbent required for effective dye removal. This relationship is primarily driven by the direct connection between the dye concentration and the availability of active sites on the adsorbent's surface. As the initial dye concentration increases, the saturation of adsorption sites on the adsorbent surface may occur, leading to a decline in the percentage of dye removal. Conversely, when the initial dye concentration is elevated, the adsorbent's capacity for dye adsorption increases. This can be attributed to the higher driving force for mass transfer associated with a concentrated dye solution (Yagub et al., 2014).

2.7 ADSORPTION ISOTHERM

An adsorption isotherm serves as a fundamental representation of the equilibrium relationship between an adsorbate in the liquid phase and the adsorbate molecules adhered to the surface of an adsorbent. This relationship is established at a constant temperature.

To fully capture the dynamic adsorptive behavior of various substances transitioning from the fluid phase to the solid phase, it is crucial to have a comprehensive description of the equilibrium state existing between these two phases that constitute the adsorption system (Ndi Nsami & Ketcha Mbadcam, 2013). The two most well-known isotherms that have been employed for describing the equilibrium of adsorption systems are the Langmuir and Freundlich isotherms.

2.7.1 The Langmuir Adsorption Isotherm.

The Langmuir isotherm is a frequently used model that can be used to explain both physical and chemical adsorptions. The assumption of this model is the idea that adsorption occurs mainly as a monolayer phenomenon. In simple terms, it implies that the surface of the adsorbent can only adsorb a single layer of molecules. This model assumes that the energy of adsorption remains constant and that adsorbate molecules are unable to move laterally or migrate over the adsorbent surface. It basically suggests there are a finite number of adsorption sites on the adsorbent surface, and that once a monolayer of adsorbate molecules occupies these active sites, no more adsorption is possible (Benjelloun et al., 2021).

The mathematical equation of the Langmuir isotherm can be written in a non-linear;

$$q_e = q_m K_L C_e 1 + K_L C_e \quad \text{.....2.1}$$

The maximum adsorption capacity corresponding to full monolayer coverage on the adsorbent surface can be calculated using the Langmuir isotherm's linear form;

$$1q_e = 1q_m + 1q_m K_L C_e \quad \text{..... 2.2}$$

Where, q_e = amount of dye adsorbed per gram of the adsorbent at equilibrium (mg/g)

q_m = maximum monolayer coverage capacity (mg/l)

C_e = equilibrium concentration of adsorbate (mg/l)

K_L = Langmuir isotherm constant (L/mg)

From the Langmuir plot of $1/q_e$ versus $1/C_e$, the values q_m and K_L can be computed from the slope and intercept respectively.

In addition, study of the Langmuir adsorption isotherm model can be stated using the dimensionless equilibrium parameter, R_L, which is described by;

$R_L = \quad 11+(1+ K_L C_e)$ …… 2.3

Where, R_L = Langmuir equilibrium parameters

C_o = initial concentration (mg/l)

K_L= constant related to the energy of adsorption, Langmuir constant (L/mg)

R_L values indicate the adsorption nature to be either unfavourable if $R_L > 1$, linear if $R_L = 1$, favourable if $0<R_L<1$ and irreversible if $R_L = 0$.qmklCe1+ $K_L C_e$.

2.7.2. Freundlich isotherm

The Freundlich isotherm is an empirical equation employed to describe the heterogeneous system. The Freundlich isotherm model is a further Langmuir model and an empirical equation for the investigation of multilayer adsorption. When using Freundlich isotherm Different kinds of various energy adsorption sites exist, but they all share the same level of entropy and are distributed according to an exponential law as a function of the heat of adsorption. Site density drops drastically over time (Benjelloun et al., 2021).

This isotherm can be represented using the nonlinear equation;

$Logq_e = logK_f + 1nlogC_e$…… 2.4

Where, q_e = amount of dye adsorbed per gram of the adsorbent at equilibrium (mg/g)

C_e = equilibrium concentration of adsorbate (mg/L)

K_f = Freundlich isotherm constant (mg/g)

n = adsorption intensity

2.8 ADSORPTION KINETICS MODELS

An effective adsorbent isn't solely characterized by its adsorption capacity; the rate of adsorption is equally vital in defining adsorbent efficiency. Understanding adsorption kinetics plays a pivotal role in assessing an adsorbent's efficiency. This is because it provides insights into the uptake rate, which dictates how long adsorbate ions reside at the solid-liquid interface.

The adsorption rate constant, a key parameter in kinetics, facilitates the comparison of different adsorbents' performance (Overah, 2021).

For the purpose of describing the mechanism of batch adsorption processes, several kinetic models have been used,

2.8.1 Pseudo first-order kinetics model

One of the most used rate equations for describing the adsorption of adsorbate from the liquid phase is the pseudo first-order kinetics model. Generally, the linear expression for the pseudo-first-order rate is;

$\log(q_e-q_t) = \log q_e - K_L t/2.303$ …… 2.5

where, q_e and q_t adsorption capacity at equilibrium and at time t, respectively (mg/g)

K_L = rate constant of pseudo first-order kinetics (min^{-1})

The plot of log (q_e-q_t) versus t should give a linear relationship from which K_L and q_e can be determined from the slope and intercept of the plot respectively.

2.8.2 Pseudo second-order kinetics model

The pseudo-second-order kinetics model can be expressed by the linear form

$tqt=1k2q_e + tq_e$ ……2.6

Where k2 (g mg-1 min-1) is the Pseudo-second- order rate constant. By plotting t/qt against t, the values of k2 and qe are determined from the graph's intercept and slope, respectively.

2.8.3 Intra-particle diffusion

It is possible that neither the pseudo-first-order kinetics model nor the pseudo-second-order kinetics model can fully explain the mechanism of solute diffusion through an adsorbent solid in some circumstances. In such situations, the intra-particle diffusion model, as developed by Weber and Morris (1963), may be used to analyze the kinetics data(Overah, 2021).

This by the Equation;

$q_t = k_{id}(t)^{0.5} + C$…….2.7

where qt is as already defined, C (mg g-1) is the adsorption constant and kid (mg g-1 min-1/2) is the intra-particle diffusion rate constant. When intra-particle diffusion is the rate- limiting step of the adsorption process, qt varies linearly with t.

2.8.4 Elovich model

The kinetics of adsorption processes can also be mathematically represented by the Elovich kinetic model. Roginsky and Zeldovich first put forth the idea in 1939, and Elovich later updated it in 1962.The model assumes that the adsorption process involves two steps: chemisorption and diffusion. Adsorption kinetics, which describes the chemical adsorption (chemical reaction) mechanism in nature, has made extensive use of the Elovich equation(Wu et al., 2009)

Initially, this model was primarily employed to investigate the sorption of gases onto solid surfaces. Over time, this foundational knowledge has been extended to liquid-solid systems, particularly in the field of aqueous phase adsorption kinetics(Overah, 2021). It is mathematically expressed as:

$q_{t = 1\ ln}(\alpha\beta) + 1lnt$……..2.8

where α (mg g -1 min-1) and β (g mg-1) are the initial adsorption rate and desorption constant, respectively. A linear plot of qt against ln(t) depicts the suitability of the model, with the slope and intercept as (1/β) and (1/β)ln(α β) respectively.

CHAPTER THREE

MATERIALS AND METHODS

3.1 MATERIALS

Table 3.1: Table of materials used

MATERIALS	SOURCE	USES
Snail shell and Floor tiles		Adsorbent
Distilled water	Biochemistry laboratory university of benin	For preparing solutions and washing of apparatus
Congo red dye	Pyrex laboratory equipment limited company	Adsorbate

REAGENTS

Table 3.2: Table of reagents used

REAGENTS	SOURCE	USES
Sodium Hydroxide (NaOH)	Pyrex laboratory equipment limited company	For regulating pH
Hydrochloric Acid (HCL)	Pyrex laboratory equipment limited company	For regulating pH
Hydrogen Tetraoxosulphate vi Acid (H_2SO_4)	Pyrex laboratory equipment limited company	For activation of the adsorbent

Table 3.3: List of equipment/apparatus.

S/N	APPARATUS	USES
1.	Beaker	It assists in the preparation of the CR stock solution
2.	Beaker	It assists in the preparation of the CR solution and also for storing of the solution
3.	UV Spectrophotometer	To measure the final concentration of the congo red dye solution in the various parameters I will be working with.
4.	Digital Weighing Balance	To measure the weight of the samples that are to be used
5.	Oven	To dry the snail shell and floor tiles thoroughly.
6.	Water Bath	To maintain the temperature.
7.	pH meter	To measure the acidity and alkalinity of the solution.
8.	Spatula	To carry the solid into their respective containers.
9.	Measuring cylinder	To measure the required volumes of liquid when preparing a solution.
10.	Volumetric Flask	Preparing the concentrations of the congo red dye from the stock solution
11.	Filter paper (What man)	To filter each sample after adsorption experiment.
12.	Tight Lid Plastic Containers	To store the prepared concentrations and activated samples to avoid contamination.
13.	Stirrer	For stirring of the solution during preparation.
14.	Sieve	To sieve the crushed absorbent fiber into fine particle size.
15.	Masking Tape	To label the containers used for easy identification.
16.	Plastic Funnel	To aid in the transferring of solution from one container to another.

3.2 METHODS

3.2.1 Preparation of Adsorbate

Congo red dye was purchased from pyrex laboratory equipment limited company, Benin city, Edo state, Nigeria. Table 2 below provides an illustration of the composition and properties of the congo red dye. 1g of CR dye was dissolved in 1L of distilled water to create a stock solution of 1g/L, which was then preserved in jars for further use. By diluting the stock solution with distilled water, several working solutions with varying concentrations of CR dye utilized in this experiment were created. Using a UV Spectrophotometer, separate examination was conducted at the maximum wavelength of 497 nm. One way to get the desired pH in each of the working solutions was to add the appropriate amount of 0.1M sodium hydroxide and 1M hydrochloric acid solution.

3.2.2 Activation of The Snail Shell And Floor Tiles

0.1M sulphuric acid (H_2SO_4) was used for activation, The powdered Snail shell and Floor tiles was impregnated with the acid in a ratio of 1:2. The mixture was stirred for even distribution of the acid throughout the powder. The impregnated snail shell and floor tiles were left for 24hrs for proper soaking. The activated powder was washed with distilled water to remove any residual acid to attain a pH of 7 (neutral).

The activated powder was dried at 150^{o}C in an oven to remove the moisture present. The activated powder was stored in an airtight container until it was ready for use.

3.3 Characterization of The Adsorbent

The Rolab Research and Diagnostic Laboratory in Ibadan received 20g of each of the activated and unactivated samples, and used a range of analytical instruments to investigate and describe them. These instruments included:

i. Fourier transform infrared (FTIR) spectroscopy
ii. Brunauer-Emmet-Teller (BET)
iii. X-ray Diffusion (XRD)
iv. X-ray Fluorescence (XRF)

3.4 Experimental procedure

3.4.1 Adsorption study

Adsorption studies were carried out in multiple locations to ascertain the effects of the variables influencing the adsorption process. to achieve the greatest dye clearance feasible. The investigation encompassed the enhancement of numerous functional elements. The initial concentration (25, 45, 65, 85, 100 mg/l), temperature (30, 35, 40, 45, 50 C), adsorbent dosage (0.5, 1, 1.5, 2,2.5 g),pH (4, 5, 7, 9, 11), and contact time (30, 55, 75, 90, 120 min) were these parameters. During each run, the values of only one parameter were changed at a time; the values of the other parameters remained the same.

The ideal value of the preceding parameter is also utilized in the ensuing runs. After the solution is filtered at the conclusion of each run, the filtrate is analyzed using a UV spectrophotometer with a maximum wave length of 497.

The % dye removal was calculated using the expression

$$\% \text{ dye removal} = \frac{C_o - C_e}{C_o} \times 100 \quad \ldots\ldots 3.1$$

Where C_0 = initial concentration of congo red (mg/l)

C_e = equilibrium concentration of congo red after adsorption in (mg/l)

3.4.2 Adsorption kinetics.

After the adsorption studies and optimum for different parameters was obtained, the kinetics of adsorption were studied using the unactivated snail shell and floor tiles. Different concentrations of dye were prepared; 25, 45, 65, 85, 100 mg/l. optimum pH of 4, and optimum dosage of 2.5g obtained from adsorption studies was used to carry out the kinetics. The kinetics of adsorption was determined by analyzing adsorptive uptake of congo red from the solution at different time intervals of 55, 90 and 120 min.

The data obtained were treated with different kinetic models such as pseudo first order, pseudo second order, intra particle diffusion model and Elovich model.

3.4.3 Adsorption Isotherm

The isotherms also of adsorption were attained using the unactivated snail shell and floor tiles. Different concentrations of dye were prepared; 25, 45, 65, 85, 100 mg/l and also an optimum pH of 4, and optimum dosage of 2.5g obtained from adsorption studies was used to carry out the isotherm. The isotherm of adsorption was determined by analyzing adsorptive uptake of congo red from the solution at different time intervals of 55, 90 and 120 min. The data obtained were treated with different isothermal models such as The Freundlich model and the Langmuir model.

CHAPTER FOUR

RESULTS AND DISCUSION

All data obtained was statistically examined using Microsoft excel and the results were presented using suitable line graphs.

The study of the effect of adsorbent dosage on adsorption of congo red dye with unactivated and activated snail shell and floor tiles gave the result below.

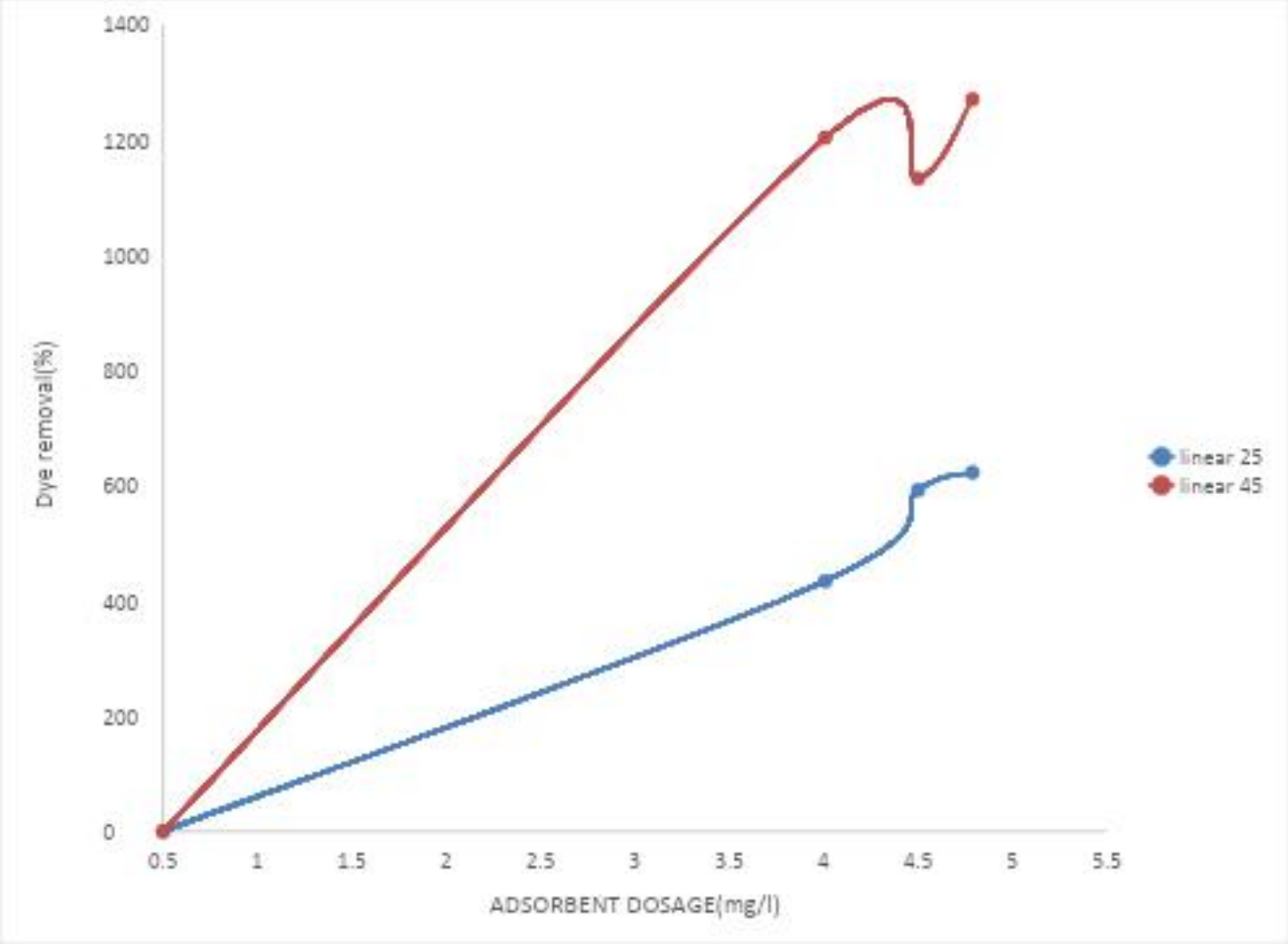


Figure 4.1: Effect Adsorbent dosage

With different amounts of the adsorbent, ranging from 0.5g to 2.5g, with 100ml of 50 mg L-1 Congo red solution at 30oc for 75min, the effect of the adsorbent quantity on Congo red adsorption was investigated. The figure above displays the experiment's findings in the form of a graph showing the amount of adsorbent dosage against % elimination for both activated and unactivated snail shell and floor tiles.The outcome demonstrates that as adsorbent dose was raised, the percentage of Congo red removed increased progressively. An optimal dosage of 2.5g of adsorbent—both activated and unactivated—was attained. For the unactivated snail shell and floor, the percentage of congo red elimination was 236.36% and 225.31%, respectively. This is because the availability of surface active sites is increased by greater doses and adsorbent aggregation.

4.2 Effect of contact time

The study of the effect of contact time on adsorption of congo red dye with unactivated and activated snail shell and floor tiles gave the result below.

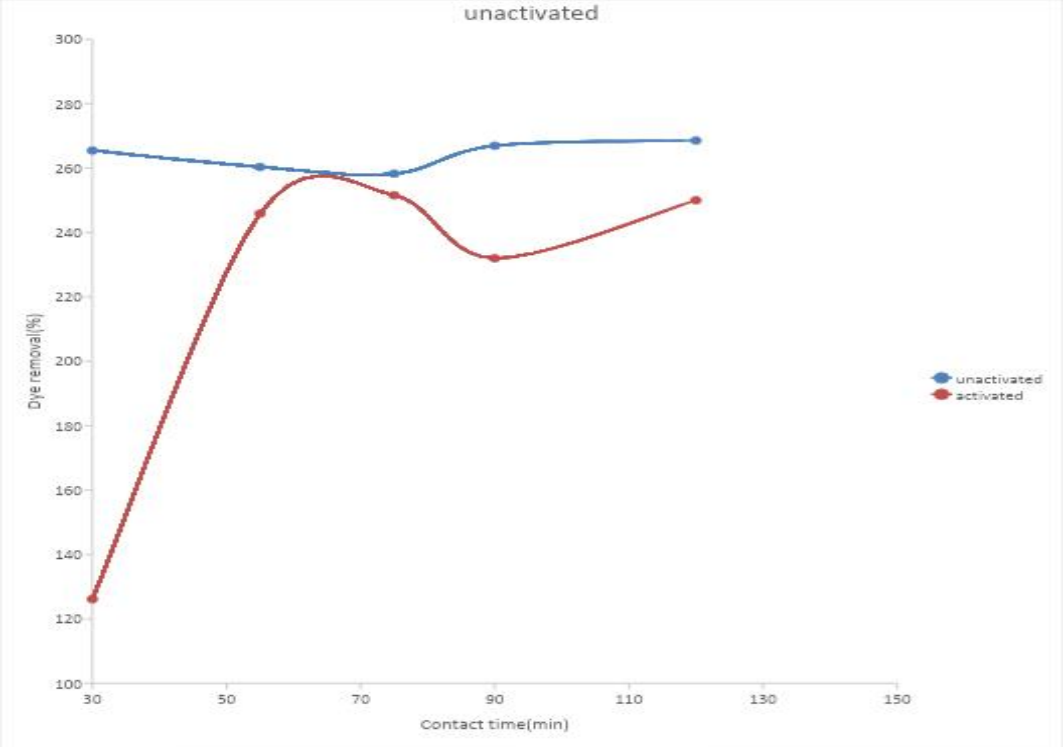


Figure 4.2: Effect of contact time **34**

The effect of contact time on Congo red adsorption was tested by contacting 2.5g of the adsorbent with 100ml of 50 mg Congo red solution at 30^{o}c for different time range of 30,55,75,90 and 120min for both activated and unactivated snail shell and floor tiles. In Figure 4.2, the study's outcome, illustrates how quickly Congo red was removed at the beginning of the process, with over 265.49 % and 126.14 % Congo red removed with unactivated and activated snail shell and floor tiles respectively within 30 min and then continued to increase gradually until reaching optimum at 120 min for unactivated and 75 min for the activated snail shell and floor tiles with an elimination of roughly 268.59% and 251.61% respectively which became nearly consistent over time. This kind of behavior is normal when the adsorbent surface has multiple adsorption sites that progressively become saturated with the dye during longer contact durations.

4.3 Effect of pH

The study of the effect of pH on adsorption of congo red dye with unactivated and activated snail shell and floor tiles gave the result below.

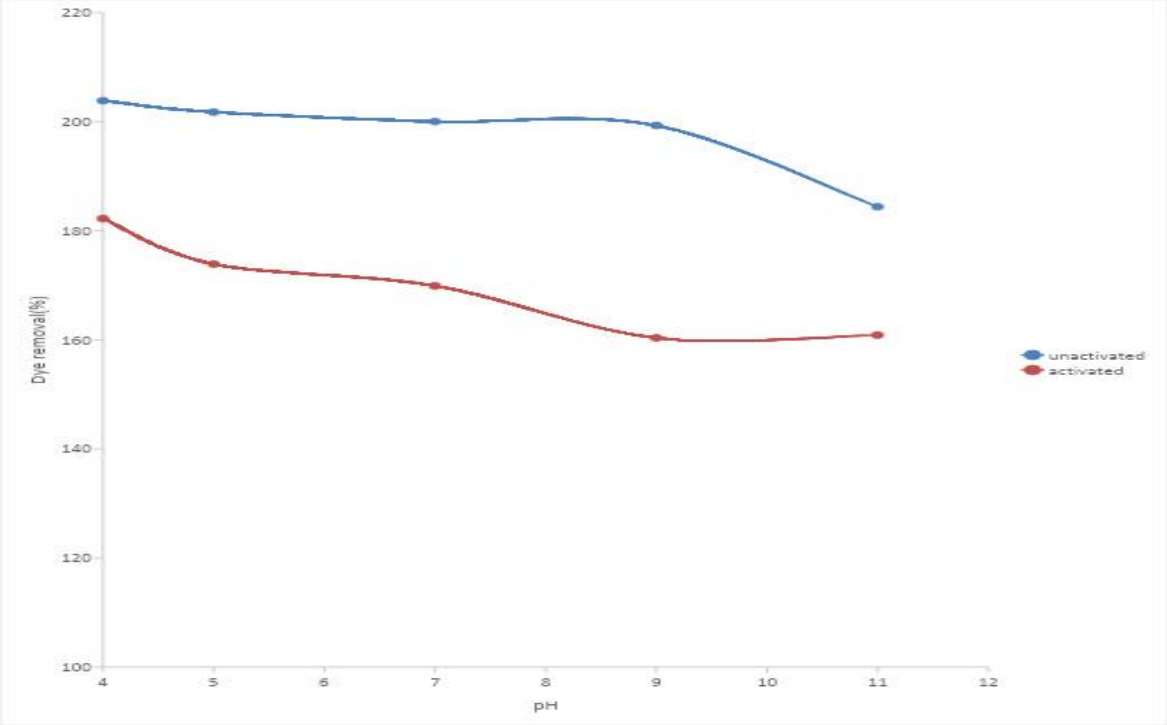


Figure 4.3: Effect of pH

The effect of the pH of the solution on the adsorption of congo red was studied by buffering the adsorptive solutions of 100ml of 50mgL^{-1} solution in the pH range of 4,5,7,9 and 11 at 30^{o}c for a contact time of 75 min, Being a dye in the diazo class, When the pH was reduced to 4.0, Congo red's color significantly changed from red to dark blue. On the other hand, the blue color of the Congo red solution changed when the pH adjusted above 6.0. The result of this study as shown in figure 4.3 for unactivated and activated indicates that 4.0 pH was the optimum for congo red removal with percentage removal of 203.86% and 182.25% for unactivated and activated snail shell and floor tiles respectively. One possible explanation for this could be because the adsorbent surfaces are protonated at an acidic pH, which promotes the anionic Congo red dye's sorption by electrostatic attraction. The absorption of the anionic dye is inhibited by electrostatic repulsion when the pH of the dye solution rises because the surface groups become deprotonated, leading to an increase in negatively charged sites. The existence of extra OH ion may account for a reduced portion of the elimination of Congo red in alkaline pH.

4.4 Effect of initial dye concentration

The study of the effect of initial dye concentration on adsorption of congo red dye with unactivated and activated snail shell and floor tiles gave the result below.

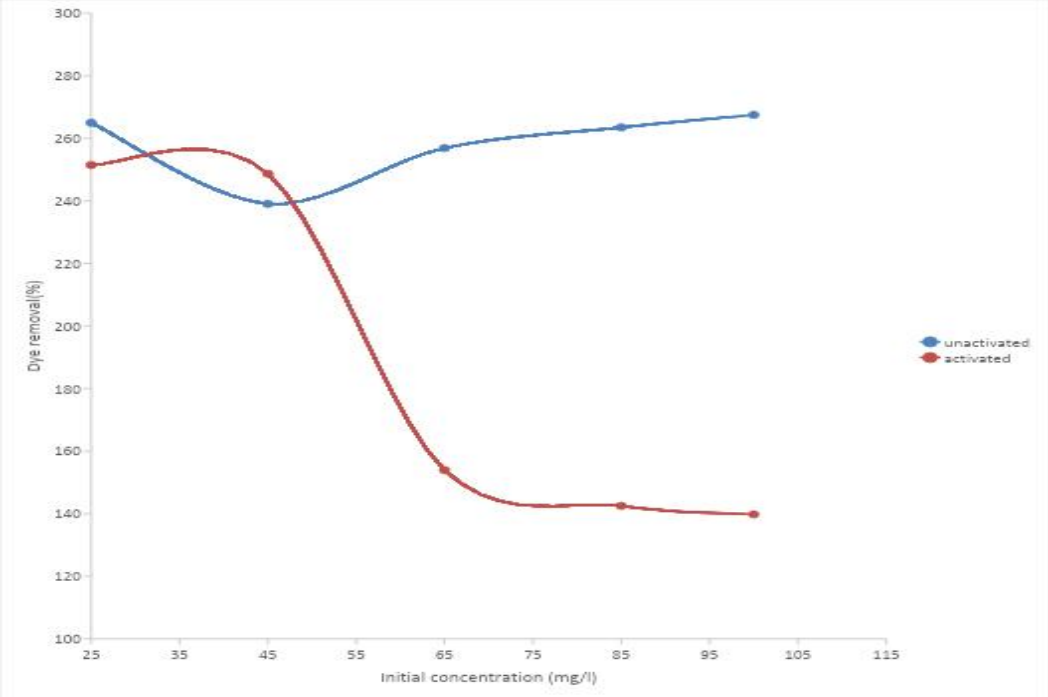


Figure 4.4: Effect of initial dye concentration

In Figure 4.4, the experimental results demonstrate that when the starting dye concentration increased from 25 to 100 mg/l, the percentage removal of congo red dyes dropped. This might be because there was less dye accessible for adsorption at a lower dye concentration in comparison to the number of active sites on the adsorbent (snail shell and floor tiles). In other words, there was a significant difference in the concentration of the adsorbent and dye. Higher concentrations made more congo red dye available, and a high initial concentration of the adsorbent is essential to overcoming the resistance of the dye molecules to bulk or mass transfer from the aqueous phase to the solid-liquid interface. The result shows that the percentage dye removal at 25mg/l is 264.96% and 251.49% for unactivated and activated respectively.

4.5 Effect of Temperature

The study of the effect of temperature on adsorption of congo red dye with unactivated and activated snail shell and floor tiles gave the result below.

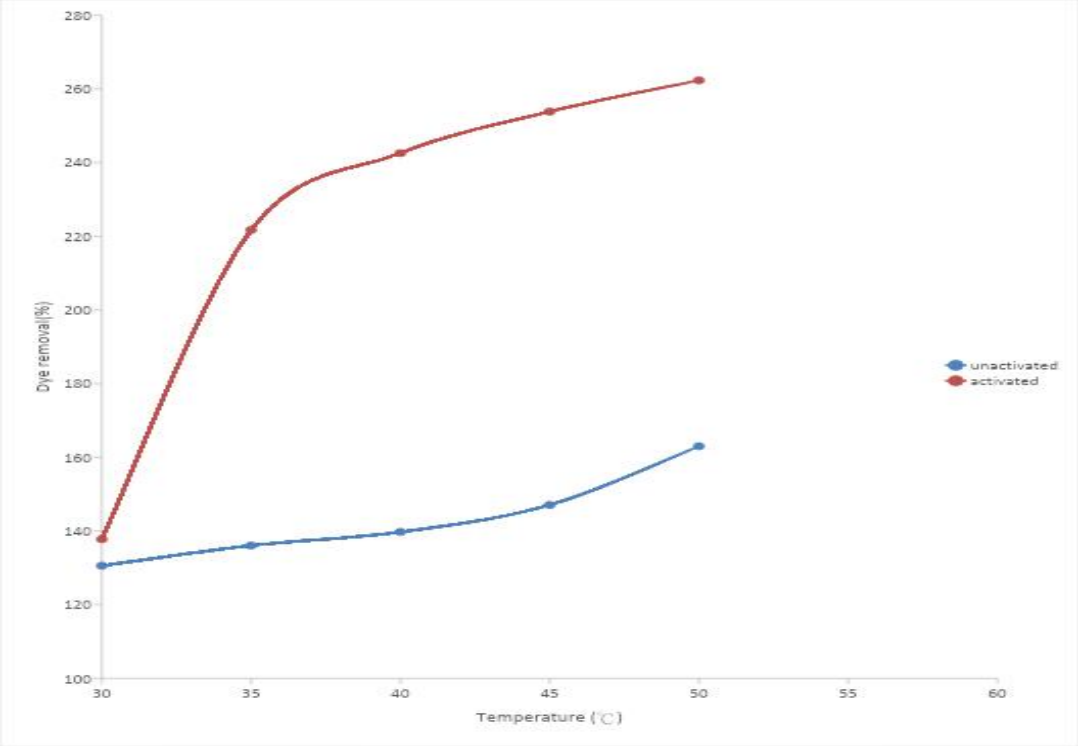


Figure 4.5 Effect of temperature

The effect of the temperature of the solution on the adsorption of congo red was studied by buffering the adsorptive solutions of 100ml of 50mgL^{-1} solution in different temperature range of 30, 35, 40, 45 and 50 at for a contact time of 75 min, The result shows that the percentage dye removal at 100mg/l are 262.32% and 163.02% for unactivated and activated respectively.

4.6 Adsorption Kinetic

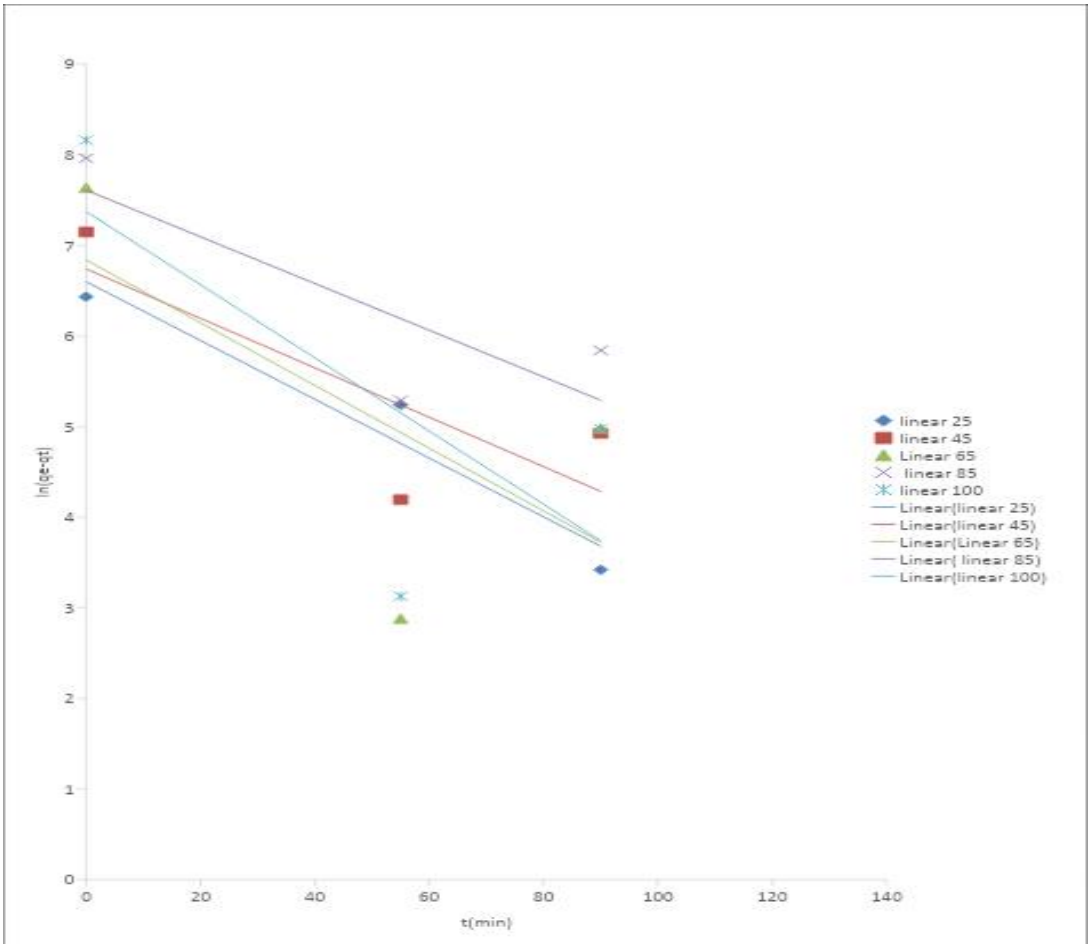


Figure 4.6: Lagergren pseudo-first order model plot for adsorption of congo red dye

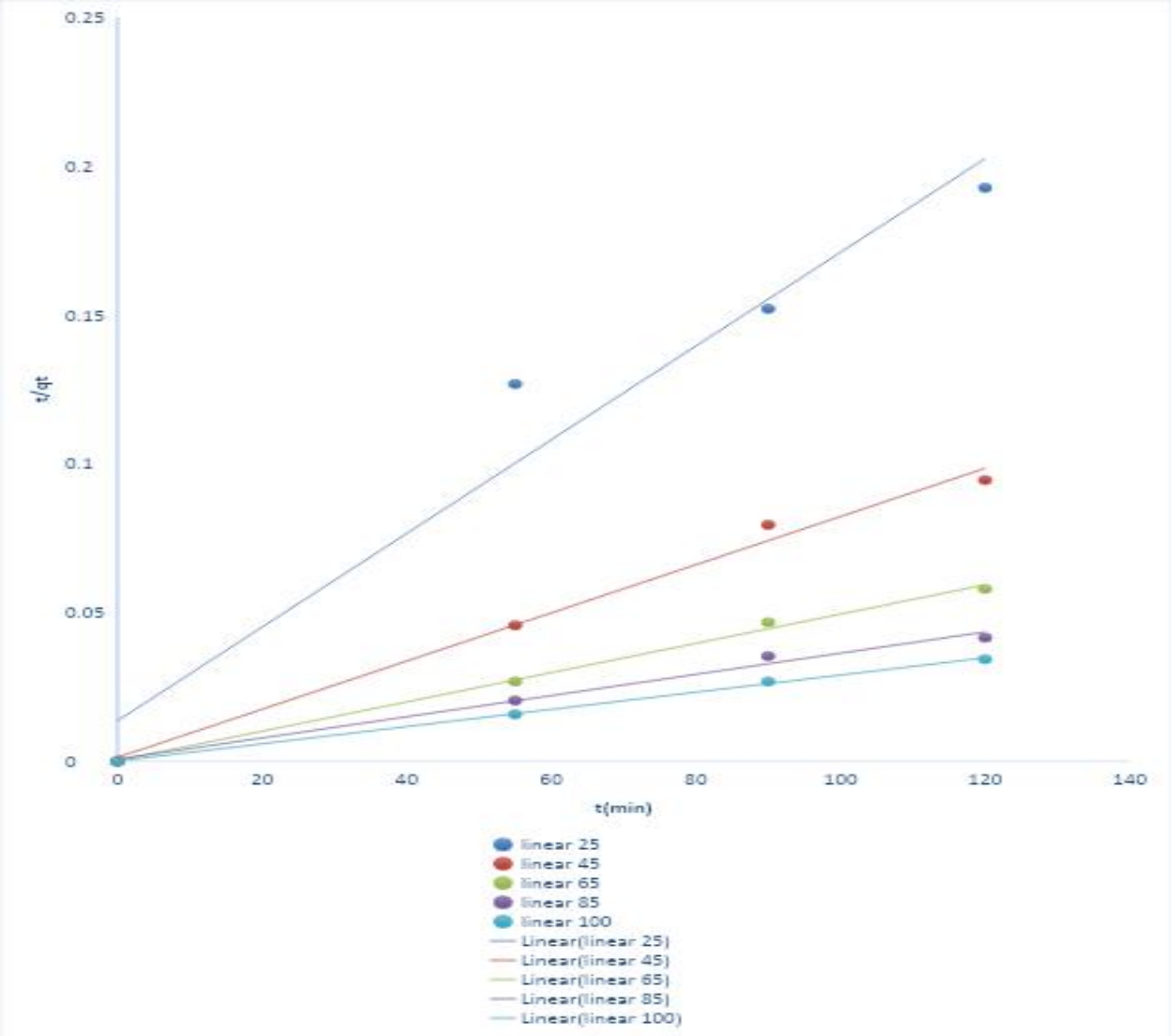


Figure 4.7: Pseudo-second order model plot for adsorption of congo red dye

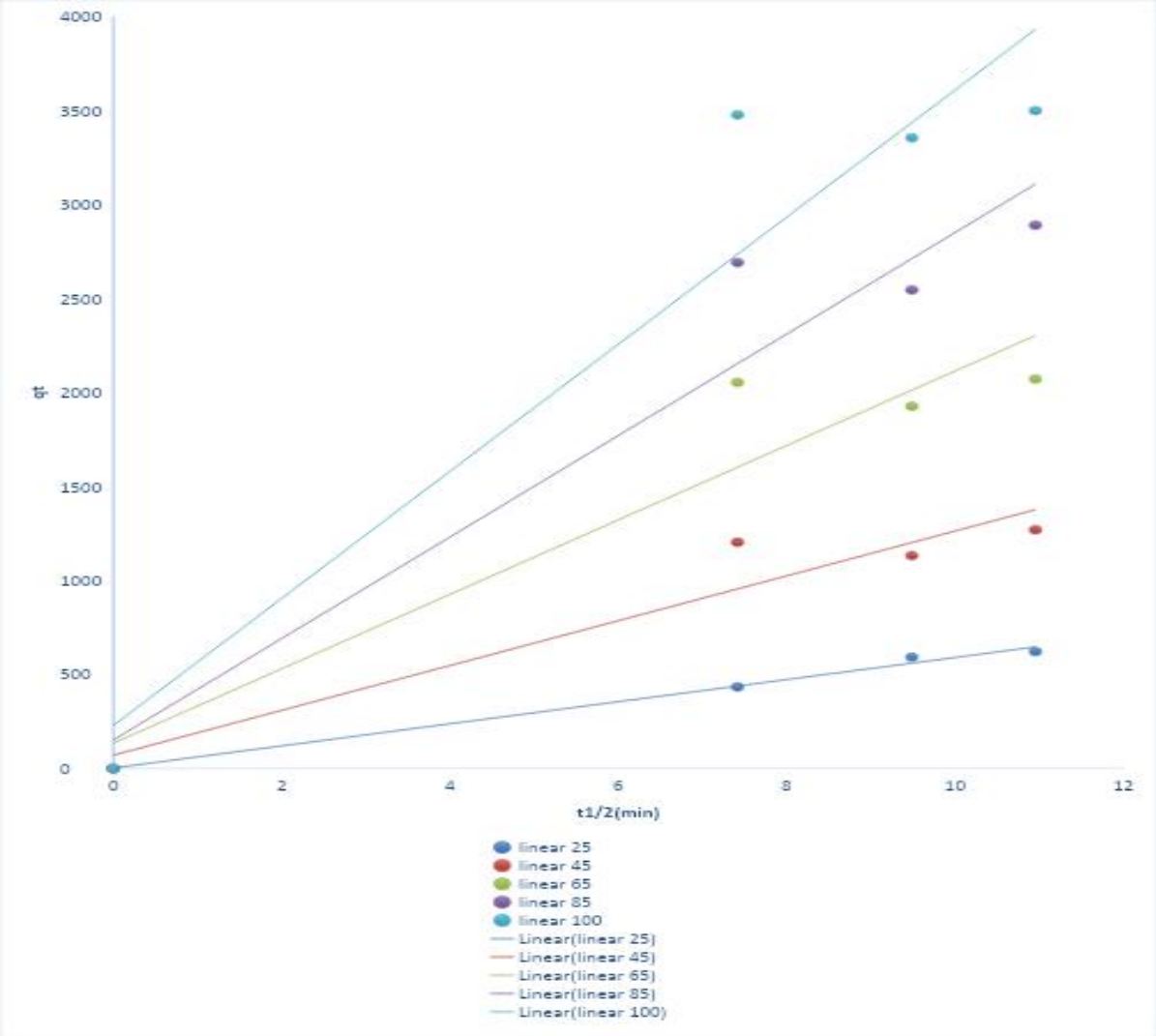


Figure 4.8: Intra particle diffusion model plot for adsorption of congo red dye

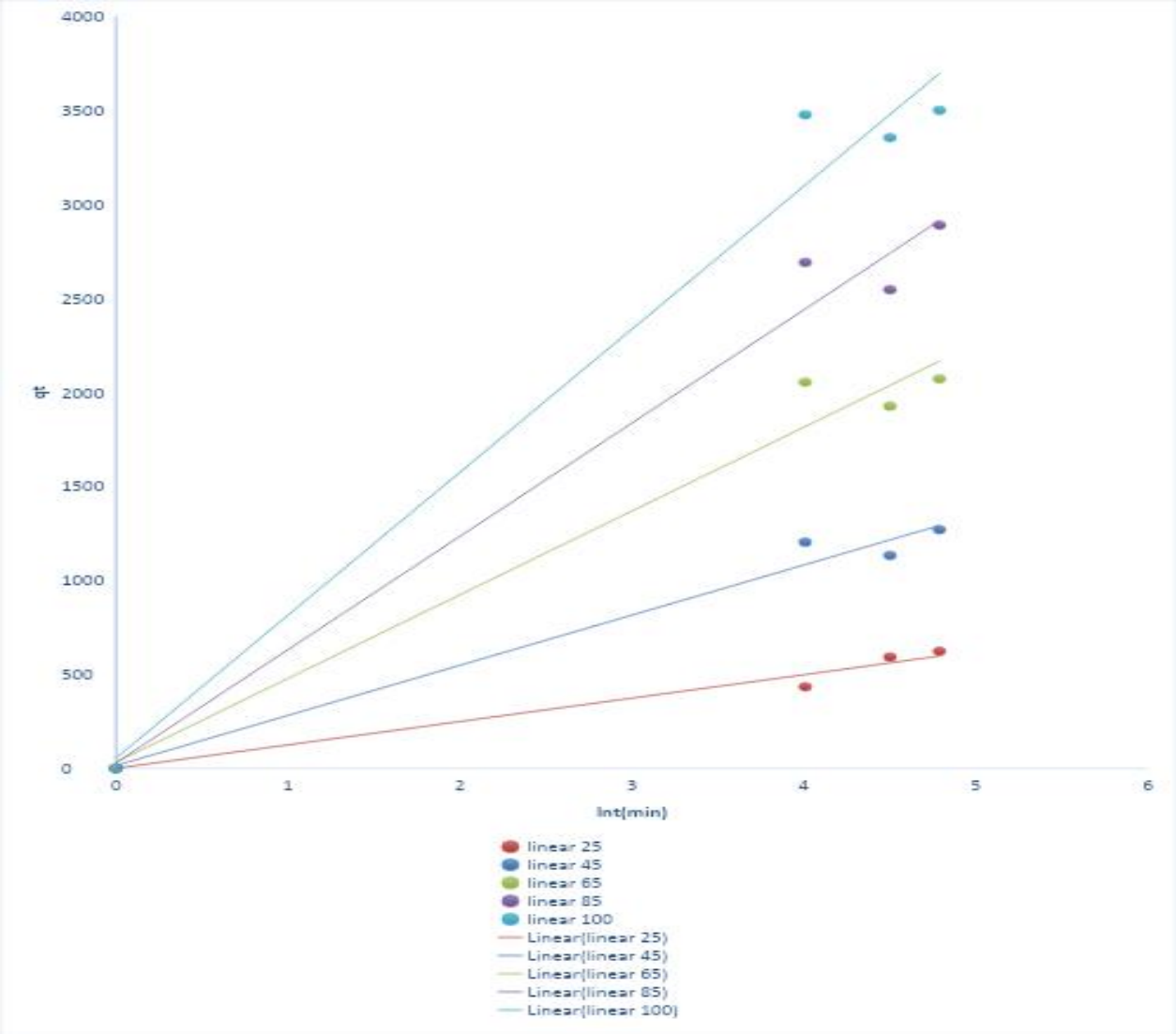


Figure 4.9: Elovich model plot for adsorption of congo red dye

4.7 Calculated constants

Table 4.1 Pseudo first order constants

Concentration (mg/l)	qe exp. (mg/g)	qe cal (mg/g)	$K_1(min^{-1})$	R-square
25	622.44	734.21	0.0324	0.9403
45	1269.56	845.22	0.0273	0.6473
65	2072.12	932.43	0.0346	0.434
85	2889.96	2017.67	0.0258	0.6885
100	3500.12	1592.08	0.0404	0.5175

Concentration (mg/l)	qe exp. (mg/g)	K_2(g/mg.min)	R-square	Qe cal
25	622.44	0.000188	0.9519	625
45	1269.56	0.000492	0.9913	1250
65	2072.12	0.000833	0.9964	2000
85	2889.96	0.000229	0.9895	2500
100	3500.12	0.0009	0.9989	3333.3

Table 4.3 Intra particle diffusion model constants

Concentration (mg/l)	qe exp. (mg/g)	Slope k.	Intercept C	R-square
25	622.44	58.777	2.7028	0.9935
45	1269.56	119.24	70.799	0.924
65	2072.12	198.01	134.32	0.9078
85	2889.96	270.03	151.23	0.9303
100	3500.12	338.07	228.63	0.9108

Table 4.4 Elovich model constants.

Concentration (mg/l)	qe exp. (mg/g)	β	α	R-square
25	0.7977	0.001314	816.46	0.9996
45	1.3391	0.001659	632.095	0.9782
65	2.005733	0.003184	478.82	0.9768
85	2.6809	0.001452	281.72	0.9847
100	3.1873	0.007890	118.20	0.9786

The kinetics of the adsorption process were assessed using contact time of 55,90 and 120min determine rate constants and equilibrium conditions using the pseudo-first-order, pseudo-second-order, and intra-particle diffusion models and Elovich model. Table 4.1, 4.2, 4.3 and 4.4 shows the kinetic constants of the calculated kinetic parameter values and the corresponding correlation coefficient derived from the four kinetic models.

The results indicated that pseudo first-order kinetic application was ineffective for dye removal by snail shell and floor tiles . This can be seen by the deviation between the experimental qe and qe calculated and also the low value of the R^2 value in Table 4.1.

The plots of the pseudo-second-order kinetics for congo red adsorption onto snail shell and floor tiles at various concentrations were tested as shown Figure 4.6 and the calculated constants in table 4.2 the result shows that correlation coefficients (R^2) for the pseudo-second-order kinetic plots were more than 0.98 which is close to unity. Also the experimental qe values did agree with the calculated qe. Intra particle diffusion model was also tested. The plot is shown in figure 4.7 and the table 4.3 shows the calculated constants. The result indicated the R^2 values were low. The Elovich model was also tested. The plot is shown in figure 4.8 and the calculated constants in table 4.4. The result indicated a high R^2 value above 0.97. Hence Only the pseudo-second-order and Elovich kinetic models of the examined kinetic models adequately fit the experimental results for congo red dyes adsorption using snail shell and floor tiles. The high R^2 values for pseudo-second-order and Elovich kinetic models is an indication of the chemisorption process with heterogeneous reaction.

4.8 ADSORPTION ISOTHERM

Langmuir model

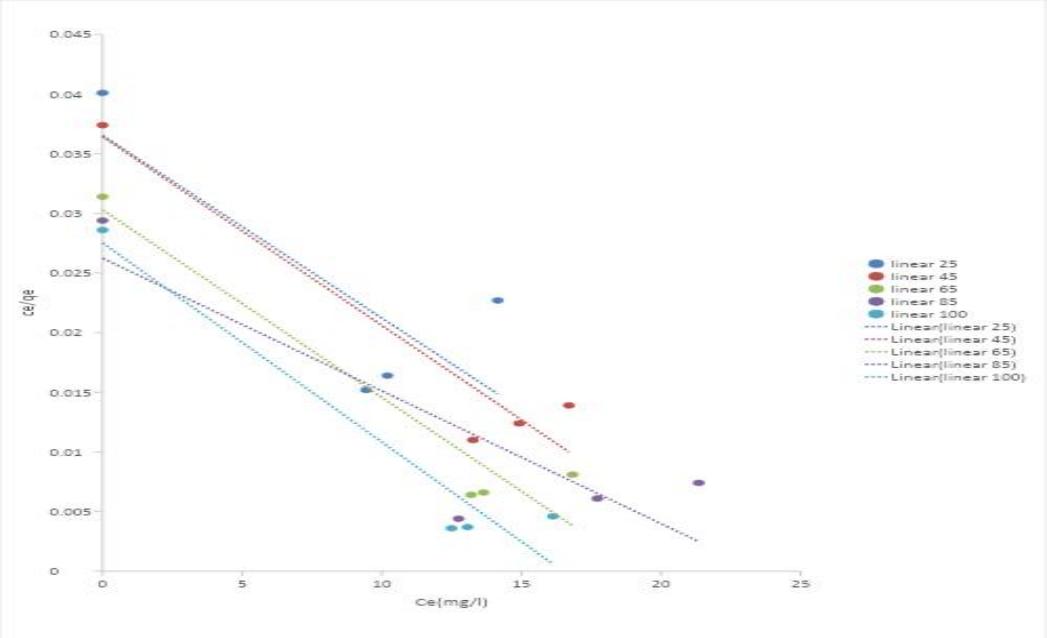


Figure 4.10: Langmuir model plot for adsorption of congo red dye

Table 4.5 Langmuir model constant

Concentration (mg/l)	qe exp. (mg/g)	qmax	k	R-square
25	0.7977	-666.667	-0.0411	0.6413
45	1.3391	-625	-0.0440	0.9235
65	2.005733	-625	-0.0528	0.9232

85	2.6809	-909.09	-0.0420	0.7769
100	3.1873	-588	-0.0618	0.9330

Freundlich Model

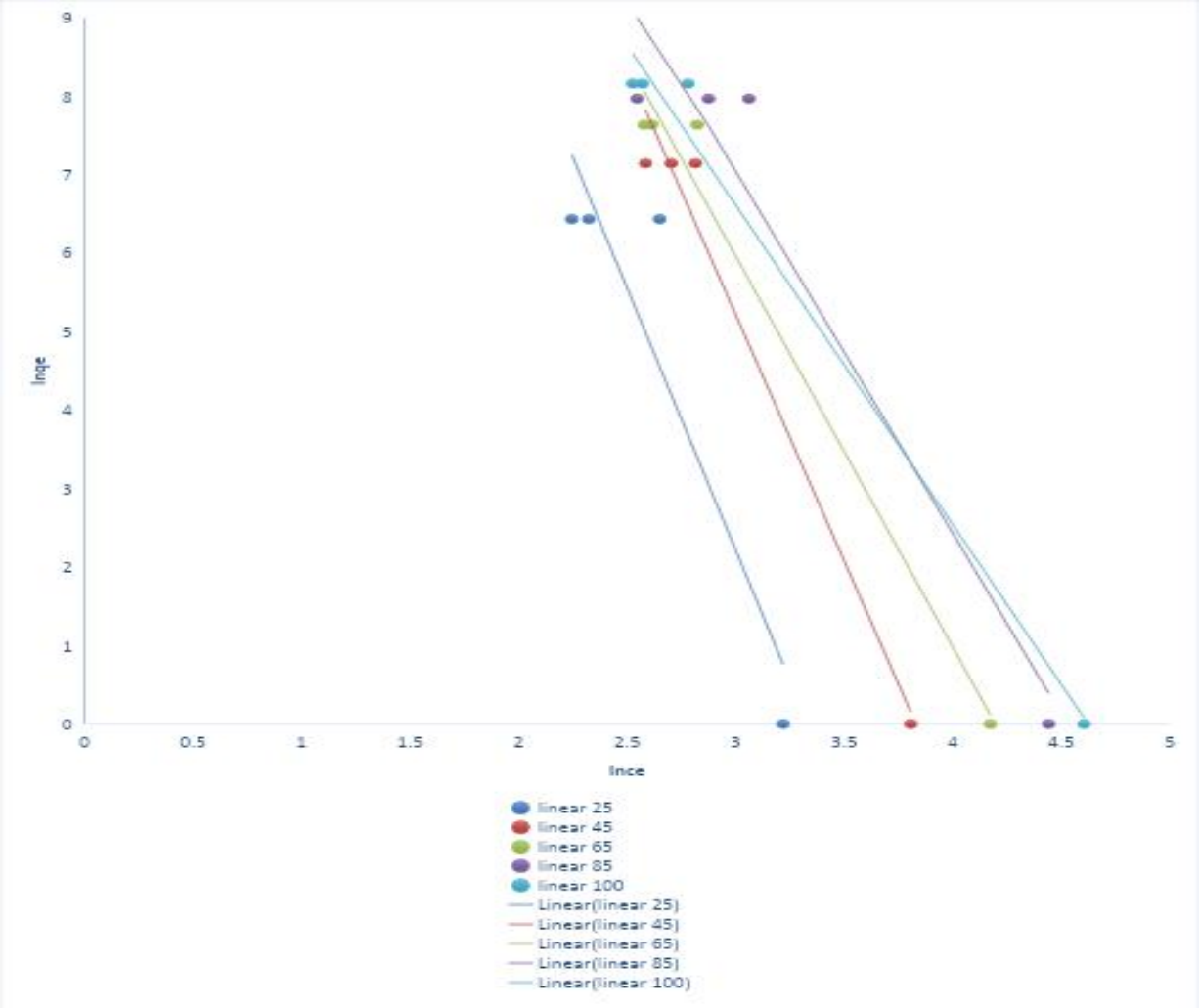


Figure 4.11: Freundlich model plot for adsorption of congo red dye

Table 4.6 freudlich model constant

Concentration (mg/l)	qe exp. (mg/g)	n	Kf	R-square
25	0.7977	-0.1499	0.00000000452	0.843
45	1.3391	-0.1593	0.00000000279	0.972
65	2.005733	-0.2007	0.00000000121	0.9798
85	2.6809	-0.2168	0.00000000117	0.9349
100	3.1873	-0.2457	0.00000000149	0.9875

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

In this study, we have examined the application of unactivated and activated snail shells and floor tiles for the removal of congo red dye from aqueous solution. From the study, the following conclusion can be made;

1. This study confirmed that the snail shell and floor tiles could effectively remove congo red from an aqueous solution.
2. The adsorbent dosage, contact time, pH of the solution and initial concentration, were all found to affect percentage dye removal for both unactivated and activated snail shell and floor tiles
3. The percentage dye removal was found to increase with increase in adsorbent dosage and contact time but decreased with increase in pH and initial dye concentration. However, the unactivated had a higher percentage at optimum of each parameter under adsorption study
4. The Optimum conditions from the adsorption studies are; Adsorbent dosage of 2.5g, contact time of 55min, pH of 4.0 and initial dye concentration of 25mg/l. At these optimum, the percentage dye removal are; Adsorbent dosage 236.36% and 225.31%, contact time 268.59% and 251.61%, pH 203.86% and 182.25%, initial dye concentration 244.90% and 251.49% and temperature 262.32% and 163% for the unactivated and activated snail shell and floor tiles respectively.
5. The outcome of the study on adsorption kinetics indicates that the pseudo-second-order kinetic model Elovich model is a more suitable choice compared to the intra particle

diffusion model and pseudo-first-order kinetic model. Hence chemisorption with heterogeneous sorption mechanism is likely to be responsible for congo red dye uptake.

5.2 RECOMMENDATION

From the study, the following recommendation is made;

1. Industrial scale use of inexpensive adsorbents, such as floor tile and snail shell, is necessary to remove dye from waste wastewater effluent
2. To enable its use in the design of adsorption columns and systems for the treatment of industrial wastewater, more research on adsorption utilizing various agricultural wastes should be conducted.

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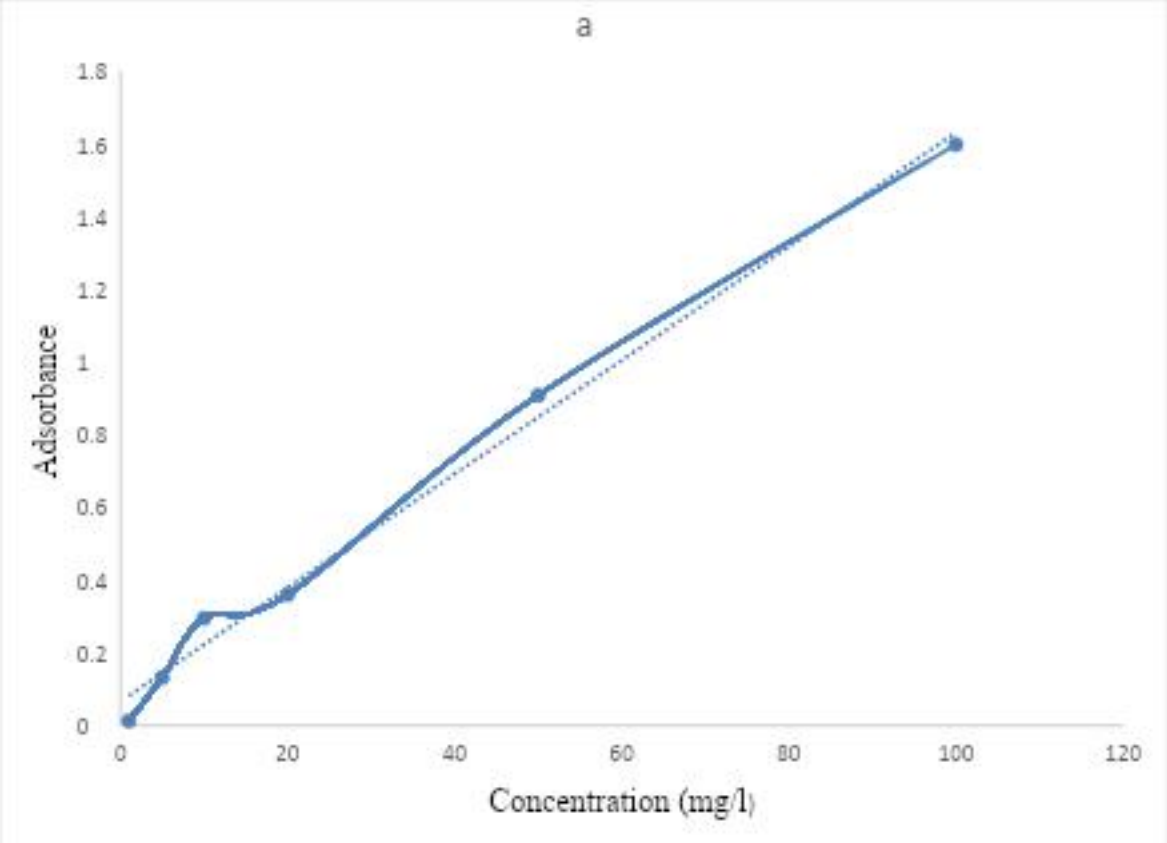
APPENDIX

CALIBRATION CURVE OF CONGO RED DYE

Wave length of congo red dye = 497nm



Congo Red Calibration curve

The equation generated from the calibration curve was used to calculate the final concentration after the adsorption process.

RESULTS FOR ADSORPTION STUDIES

Effect of Adsorbent dosage (unactivated)

Effect of adsorbent dosage			
Adsorbent Dosage	Absorbance value	Concentration	Percentage dye removal
0.5	0.091	30.35	229.50
1	0.047	28.64	249.16
1.5	0.030	27.98	257.40
2	0.053	28.88	246.26
2.5	0.075	29.73	236.36

Effect of Adsorbent dosage (activated)

Effect of adsorbent dosage			
Adsorbent Dosage	Absorbance value	Concentration	Percentage dye removal
0.5	0.769	56.63	76.58
1	0.212	35.04	185.39
1.5	0.003	26.94	271.20
2	0.090	30.31	229.92
2.5	0.101	30.74	225.31

Effect of Contact time(Unactivated)

Effect of contact time			
Time(min)	Adsorbance value	Concentration	Percentage dye removal
30	0.014	27.36	265.49
55	0.024	27.75	260.36

75	0.028	27.91	258.29
90	0.011	27.25	266.97
120	0.008	27.13	268.59

Effect of Contact time (activated)

Effect of contact time			
Time(min)	Adsorbance value	Concentration	Percentage dye removal
30	0.449	44.22	126.14
55	0.054	28.91	245.90
75	0.042	28.44	251.61
90	0.085	30.12	232.00
120	0.045	28.57	250.01

Effect of pH (Unactivated)

Effect of pH			
pH	Adsorbance value	Concentration	Percentage dye removal
4	0.157	32.91	203.86
5	0.163	33.14	201.75
7	0.168	33.33	200.03
9	0.170	33.41	199.31
11	0.215	35.16	184.41

Effect of pH (activated)

Effect of pH			
pH	Adsorbance value	Concentration	Percentage dye removal
4	0.22	35.43	182.25
5	0.25	36.51	173.89
7	0.264	37.05	169.91
9	0.299	38.41	160.35
11	0.297	38.33	160.89

Effect of initial dye concentration (Unactivated)

Effect of concentration			
Initial concentration	Adsorbance value	Concentration	Percentage dye removal
25	0.015	27.40	264.96
45	0.069	29.49	239.09
65	0.031	28.02	256.88
85	0.018	27.51	263.50
100	0.010	27.21	267.51

Effect of initial dye concentration (activated)

Effect of concentration			
Initial concentration	Adsorbance value	Concentration	Percentage dye removal
25	0.042	28.45	251.49
45	0.048	28.68	248.68
65	0.324	39.38	153.94
85	0.372	41.24	142.48
100	0.384	41.71	139.75

Effect of temperature (activated)

Effect of concentration			
Temperature	Adsorbance value	Concentration	Percentage dye removal
30	0.427	43.37	130.57
35	0.401	42.36	136.071
40	0.384	41.71	139.75
45	0.352	40.47	147.09

50	0.289	38.02	163.02

Effect of temperature (unactivated)

Effect of concentration			
Temperature	Adsorbance value	Concentration	Percentage dye removal
30	0.393	42.05	
35	0.110	31.08	221.74
40	0.061	29.19	242.58
45	0.037	28.26	253.86
50	0.0215	27.66	262.32

The concentrations after adsorption process were extrapolated using the equation generated from the calibration curve.

Y = 0.015X – 0.0622 ……. A1

Where Y = the absorbance values obtained from the spectrophotometer after adsorption.

X = the final concentration (mg/l)

The % dye removal was calculated using:

% dye removal $= \frac{Co-Ce}{Co} \times 100$……A2

Where Co and Ce are the initial and final concentrations.

RESULTS FOR ADSORPTION KINETICS

The experiment was done at constant temperature of 30^{o}C

Adsorption kinetics (Co=25mg/l)

Time	Absorbance	Ct	qt	qe	ln(qe-qt)	t/qt	$t^{1/2}$	lnt
0	0	0	0	622.44	6.4336	0	0	0
55	0.156	14.153	433.88	622.44	5.2394	0.1268	7.4162	4.00733
90	0.094	10.203	591.88	622.44	3.4197	0.1521	9.4868	4.4998
120	0.082	9.439	622.44	622.44		0.1928	10.9545	4.7875

Adsorption kinetics (Co=45mg/l)

Time	Absorbance	Ct	qt	qe	ln(qe-qt)	t/qt	$t^{1/2}$	lnt
0	0	0	0	1269.56	7.1464	0	0	0
55	0.168	14.917	1203.32	1269.56	4.1938	0.0457	7.4162	4.00733
90	0.196	16.700	1132.00	1269.56	4.9241	0.0795	9.4868	4.4998
120	0.142	13.261	1269.56	1269.56		0.0945	10.9545	4.7875

Adsorption kinetics (Co=65mg/l)

Time	Absorbance	Ct	qt	qe	ln(qe-qt)	t/qt	t1/2	lnt
0	0	0	0	2072.12	7.6363	0	0	0
55	0.148	13.643	2054.28	2072.12	2.8814	0.0268	7.4162	4.00733
90	0.198	16.828	1926.88	2072.12	4.9783	0.0467	9.4868	4.4998
120	0.141	13.197	2072.12	2072.12		0.0579	10.9545	4.7875

Adsorption kinetics (Co=85mg/l)

Time	Absorbance	Ct	qt	Qe	ln(qe-qt)	t/qt	t1/2	lnt
0	0	0	0	2889.96	7.9600	0	0	0
55	0.212	17.719	2691.24	2889.96	5.2912	0.0204	7.4162	4.00733
90	0.269	21.350	2546.00	2889.96	5.8405	0.0353	9.4868	4.4998
120	0.134	12.751	2889.96	2889.96		0.0415	10.9545	4.7875

Adsorption kinetics (100mg/l)

Time	Absorbance	Ct	qt	qe	ln(qe-qt)	t/qt	t1/2	lnt
0	0	0	0	3500.12	8.1605	0	0	0
55	0.139	13.070	3477.2	3500.12	3.1268	0.0158	7.4162	4.00733
90	0.184	16.127	3354.92	3500.12	4.9773	0.0268	9.4868	4.4998
120	0.130	12.497	3500.12	3500.12		0.0343	10.9545	4.7875

qt and qe represent the amount adsorbed at time interval and equilibrium, it was calculated using:

$qe = \frac{v\,(Co-Ce)}{W}$ …… A3

$qt = \frac{v\,(Co-Ct)}{W}$ ……..A4

Where, V = volume of congo red dye solution (L) which is 100 ml (0.1L).

W = weight of the dry adsorbent dosage (3.0 g)