KINETICS AND ADSORPTION OF THYMOLPHTHALEIN DYE ON HYDROTHERMALLY ACTIVATED RICE HUSKS

BY

ABUKWI PATIENCE PERUTH

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SUPERVISOR

DR. KIGOZI MOSES

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DECLARATION

I Abukwi Patience Peruth declare that the information here is my original work to the best of my knowledge and references have been cited where information from other people's work was used. The work has never been submitted to any other institution for any award or publication.

Signature..... date.....04/09/24.....

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APPROVAL

This work has been supervised and approved by Dr. Kigozi Moses

Signature..... Date.04/09/2024

Dr. Kigozi Moses

Lecturer

Chemistry department

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DEDICATION

I dedicate this project to my family for their help during the research time both financially and any other way to make the research possible and making me reach where I am.

ACKNOWLEGDEMENT

I want to thank the almighty God for continuously guiding me throughout this project and glory goes back to him. My sincere appreciation to my supervisor Dr. Kigozi Moses for his parental efforts, guidance and words of encouragement that made me successfully complete this project, May the Almighty God bless you abundantly. The chemistry department of Busitema University for making it possible for me to complete my project. Not forgetting Madam Amado Mary who was always there whenever I needed her. All the chemistry majors Busitema University 2021-2024 especially Anyait Salome, Wazemba Bonifance, Nambuba Esther, Bwire Ivan and Ssemugenyi Edison words can't express my gratitude but am very grateful for your help. The family members Mr. Omulepu Ezra, Mrs. Omulepu Theopista Awor, my sister Alukudo Gloria, Oputo Etyang David, madam Nyachwo Toscana, Mr. Oputo Samuel, thanks for your support in my education and may God bless you abundantly.

ACRONYMS USED IN THE TEXT

RHA-rice husk ash

RH- rice husk

RHC-rice husk carbon

pH- potential of hydrogen

FTIR- Fourier transform infra-red

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ABSTRACT

RHC, Rice husk carbon (activated rice husk) has the ability to adsorb the dye stuff from aqueous solution. It may be a useful low cost adsorbent for the treatment of effluents, discharged from textile industries. In this study, adsorption was used on the removal of thymolphthalein indicator from water using activated rice husks. The influence of contact time, adsorbent dose and initial dye concentration on activated rice husks was evaluated on the sorption capacity. The tests were determined in batch. Analytical measurements were performed by uv-vis spectroscopy. Activation of rice husks was done hydrothermally using an autoclave reactor at a temperature of $180^{O}C$. Chemical and morphological characteristics of the activated rice husks were evaluated using thermogravimetric analysis and infrared spectroscopy. Sorption kinetics were conducted and they followed the first pseudo order kinetic model with R^2 value of **0.9743** which was higher than that of the second order kinetic model. Equilibrium data was represented well by the freudlinch model with R^2 value of **0.997** than the Langmuir model.

CHAPTER ONE

1.1. Bbackground to the study

More than 71% of the earth's surface is covered by water, but only a slight portion (less than 1%) of this huge reserve is fit for drinking purposes due to various contaminations and pollution (Singh, Nagpal, & Sonal, 2018). Globally, water pollution is a serious issue. A huge quantity of water is polluted every year that is discharged into the environment. The leading cause of water pollution comprises the discharge of unprocessed industrialized and unindustrialized effluents and municipal wastes which includes various poisonous and harmful contaminants such as dyes, heavy metals, pesticides, inorganic and organic pollutants (Tholiso, 2016).Over the past few decades, cosmetic, dyeing, printing, painting, textile, petroleum and paper industries are rapidly expanding that produce a large amount of dye polluted water (Shahin, Niharika, & Zarie, 2020). This results in severe deterioration of worldwide water quality, largely owing to unrestrained usage of water, fast-growing development, and unintended urbanization (Schwarzenbach, Egil, Hofstetter, & Wehrli, 2010).

Dyes are toxic pollutants, which impart color to water when discharged into aqueous systems. Thus, the presence of dyes in water even at trace concentrations (1.0 mg/L) makes water undesirable for human consumption (Sasureka, Roy, & Mallick, 2021). Various types of noxious dyes are present in wastewater in large quantities originating from different industrial activities; and contributing to some 0.7 million tons of dyes annually (Zhou, Zhou, & Yongdi, 2019). The textile industry alone contributes to a wide pollution range as 1.0 kg of textile processing consumes more than 100 L of water (Yadav, Yadav, & Bagotia, 2021)

They are carcinogenic and toxic in nature and even some are non-biodegradable (Mittal, Dash, Srivastava, & Yadav, 2021). Their presence aqueous systems is directly linked to allergies, heart-related problems, mutations, skin irritations, and tumors. (Dai, Sun, Wang, & Zhang, 2018)

The fashion industry is responsible for up to 10% of global greenhouse gas emissions and is a major cause of water pollution worldwide (European Topic Centre on Waste and Materials in a green Economy, 2019),with over 80% of its supply chain impacts on the environment taking place in Global South countries where the majority of clothes are manufactured (European Environmental Agency, 2019) .But this isn’t even the only serious consequence of the fast

fashion industry on the Global South, vast quantities of polluting textile waste from the fast fashion industry is increasingly making its way to Global South countries. Because of these massive negative impacts on the environment, “circularity” has become the buzzword among global fashion brands trying to clean up their image. But circularity is virtually non-existent in the fashion industry; while less than 1% of clothes are recycled into new clothes, garment production volumes are growing by 2.7% annually (Andrew Brooks(2015), 2015)

The main aim of this research is to help gain insight into the adsorption process and efficiency of dyes in the treatment of water containing textile pollutants especially dyes. This will help in regulating the water quality, minimising health impacts and also help local manufacturers of clothing in such a way that they are able to manufacture their own dyes thus minimising expenditure.

1.2. Statement of the problem

The treatment of wastewater tainted with dyes is the current issue due to the increase in pollution more so water pollution from textile and dyeing industries. A significant amount of colored wastewater is released into the environment as a result of the widespread use of dyes in the textile, printing, paper, and leather industries. These dyes' toxicity, bioaccumulation potential, and persistence make them a serious hazard to both human health and aquatic environments. The physical and chemical techniques used in the current wastewater treatment processes are frequently insufficient to remove colors from wastewater in an efficient manner. It can be difficult to remove dyes because many of them are stable in water for long periods of time and are resistant to degradation. Due to the above aspects, there is a need to understand the kinetics and adsorption mechanisms of dyes on activated samples such as rice husks, orange peels among others to come up with a more efficient mechanism of dye adsorption which can be applied in wastewater treatment. This can help in minimising the effects that may arise from dye disposal into water bodies. Implementing effective dye removal methods could allow local textile industries to produce their own clothing, rather than relying on imported products.

1.3. Objectives of the study

1.3.1. Main objective;

The main objective of this study was to aactivatee rice husks hydrothermally, analyzing their properties and evaluating their ability and effectiveness as low cost adsorbents in absorbing thymolphthalein dye through kinetics and adsorption experiment.

1.3.2. Specific objectives

The main objective can be achieved through the following specific objectives;

i. To carry out hydrothermal Activation of rice husks.
ii. To characterisee rice husks using the Fourier transform infra-red analysis
iii. To set up and carry out the adsorption experiment
iv. To perform the kinetics and adsorption of thymolphthalein adsorbate on rice husks as the adsorbent.

1.4. Justification of the study

The research is carried out in order to address the environmental concerns, understanding the kinetics of adsorption of activated rice husks on thymolphthalein dye which is essential in designing efficient water treatment processes, sustainable and scalable solutions for water treatment. This is important in maintaining the environment and also reducing hazards that may arise due to textile disposal of dyes into water streams.

CHAPTER TWO

2.1. Literature review

2.1.1. Dyes

The textile finishing dyes are organic compounds capable of absorbing the light radiation in the visible range of the spectrum and of reflecting or diffusing supplementary radiation on the other hand, and dyeing a substance in a sustainable manner on the other hand (sin, wan, & siew, 2020).

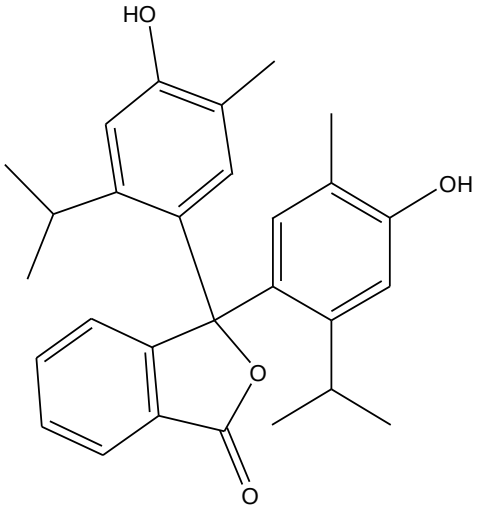
2.1.1. a. Thymolphthalein

Thymolphthalein is a widely used indicator dye that is commonly used in analytical chemistry and biochemical experiments. It is known for its ability to change colour in response to changes in pH, making it an ideal candidate for studying adsorption processes. Understanding the kinetics and adsorption behaviour of thymolphthalein by hydrothermally activated rice husks is crucial for exploring its potential as an adsorbent material in various applications, such as pH sensors and water treatment.

Chemical formula;

$C_{28}H_{30}O_4$

Structure;



thymolphthalein figure 1

There are two classifications of dyes;

2.1.1.1. Chemical classification;

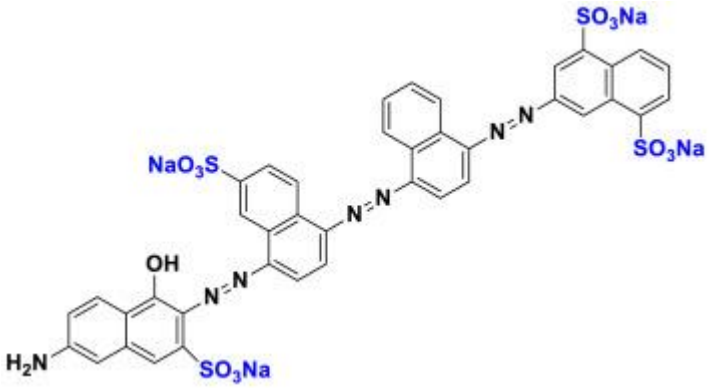
It is based on the chemical structure of the dyes and more particularly on the nature of their chromophore groping, such that dyeing plants will be able to predict the chemical reactions between the dye and the reducing agents, the oxidants and the other compounds (Mansour, Boughzalaa, & Dridi, 2011). They include;

(a). Azo dyes

They constitute the largest family, including 70% of the world's annual production of synthetic dyes (Rajasimman, Venkatesh Babu, & Rajamohan, 2017). They are characterised by the presence of one or more azo groups (N=N) linked to the –OH or –NH2 type auxochrome groups. The table below shows some of the examples of azo dyes;

Table 1. Chemical structures and maximum wave lengths (λ_{max}) of some azo dyes.

Dyes	**Chemical structures**	**λ_{max} (nm)**	**Groupings**
Yellow reactive 4 (YR4)		385	monoazo

Dyes	Chemical structures	λ_{max} (nm)	Groupings
Black reactive 5 (BR5)		590	disazo
Direct blue 71 (DB71)		575	triazo

(b). Anthroquinone dyes;

They are the most important dyes after azo dyes. Their chemical formulas derived from anthracene show that the chromophore group is a Quinone nucleus to which hydroxyl or amino groups can be attached (Franciscon, Zille, Isis, Durraant, & Fabiana, 2009). This group gives the dye molecule good light resistance. The table below lists some of the examples of anthhroquinone dyes;

Table 2. Chemical structures and λ_{max} of some anthraquinone dyes.

Dyes	Reactive blue 19 (RB19) remazol brilliant blue r	Acid blue 62 (AB62)
Chemical structures		
λ_{max} (nm)	592	635

2.1.1.2. Water soluble dyes

(a) Acid or anionic dyes

They are also called anionic dyes used for the dyeing of fibres which contain an amino group (NH_2) such as wool, polyamide, silk and mod acrylic which should be fixed on the NH_4^+ cations of these fibres in acid medium. They consist of a chromophore group and one or more sulphonates groups allowing their solubilisation in water (Pisoni, Marluza Pereire, & Cesar Liberato, 2013). Most of these dyes are azo, anthraquinone or triarylmethanes (Alkan, Celikcapa, Demirbas, & Dogan, 2005)

(b). Basic dyes or cationic dyes

They are also called cationic dyes which are salts of organic bases capable of directly dyeing the fibres bearing anionic sites and the cost only after treatment with metal salts. They are composed of diarylmethane, triarylmethane, anthraquinone and/or azo structures (Eseoghene H, Moses G, Jane C, & Omatayo A, 2016)

(**c). Reactive dyes**

Reactive dyes contain chromophore groups mainly derived from azo, anthraquinone and phthalocyanine families (Dusan Z, Milka L, Antonije E, & Branimir N, 2012). Their name is linked to the presence of a reactive chemical function, of the triazine or vinyl sulfone type, ensuring the formation of a strong covalent bond with the fibres (Sing Lai, Wan Loy, & Siew Moi, 2010). They are more soluble in water and in the dyeing of cotton and possibly in that of wool and polyamides.

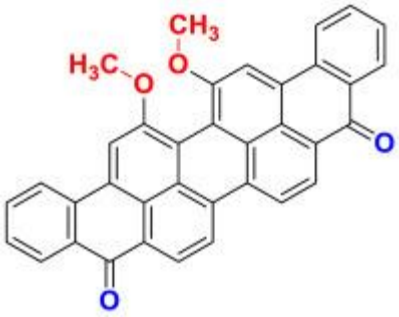
2.1.1.3. Insoluble dyes in water

(a). Vat dyes

The vat dyes are water-insoluble dyes when they are fixed on the fibres, but they become soluble and substantive by the reduction in very alkaline medium (in vat) in leuco-derivatives soluble in water (Chakraborty, 2010). They are then re-solubilized by oxidation in air or with the aid of an oxidizing agent and are generated within the fibre, on the other hand (Burkinshaw & Young A, 2010). They are known for their good resistance to degradation agents (washing

and solar rays) and their affinity for certain fibres such as cotton, linen, wool, silk, rayon and other cellulosic fibres such as indigo for dyeing jeans (or denim). The table below shows some of the vat dyes;

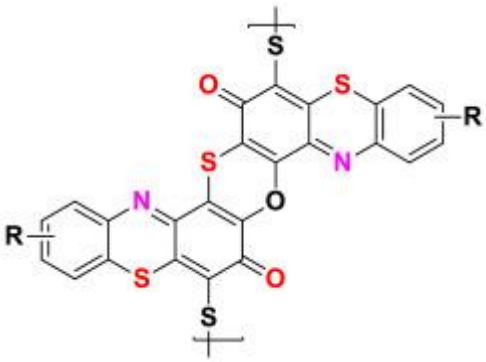
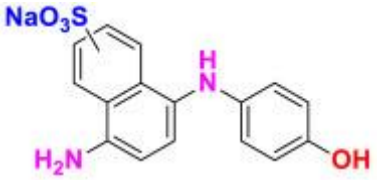
Table 3. Chemical structures and λ_{max} of some vat dyes.

Dyes	**Blue indanthrene RS**	**Vat green 1**
Chemical structures		
λ_{max} (nm)	631	630
Groupings	anthraquinonique	anthraquinonique

(b). Sulfur dyes

Sulfur dyes are quite similar to vat dyes by the method of use, but they represent sulfur-containing molecules and have different chemical structures with high molecular weight (Chaari, et al., 2009). They are insoluble in water but applied as a soluble derivative after reduction in an alkaline medium by sodium sulphide. They are then reoxidized to their insoluble state in the fibre. Sulfur dyes are typically applied to cotton to produce cost-effective dark shades with a medium to good wash and light fastness. Table 5 lists some examples of sulfur dyes (Mahir, Sermet, Ozkan, & Dogan, 2005)

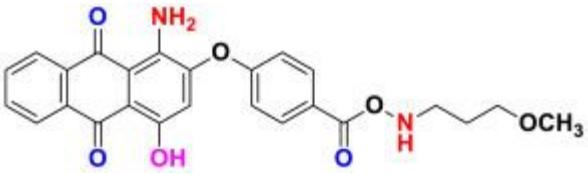
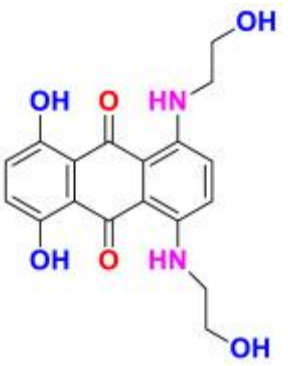
Table 5. Chemical structures and λ_{max} of some sulfur dyes.

Dyes	Sulfur black (SB)	Sulfur blue 15 (SB15)
Chemical structures		
λ_{max} (nm)	597	593

(c). Disperse or dispersible dyes

They are also called plastosolubles, examples of which are shown in table 6, which are very insoluble in water and applied as a fine powder dispersed in the dye bath (Muzamil, et al., 2017). They are stable during at high temperature dyeing, to diffuse in the synthetic fibres and then to fix it. Disperse dyes are widely used in the dyeing of most manufactured fibres, especially polyester and polyamide in the presence of a dispersing agent that is always added to the solution (Rajasimman, Venkatesh Babu, & Rajamohan, 2017).

Table 6. Chemical structures and λ_{max} of some disperses dyes.

Dyes	Red disperse60 (RD60)	Blue disperse 7 (BD7)
Chemical structures		

Dyes	Red disperse60 (RD60)	Blue disperse 7 (BD7)
λ_{max} (nm)	536	570
Groupings	anthraquinonique	anthraquinonique

(d). Pigments

The pigments are coloured compounds that are insoluble in water, in the solvent (basic and acidic) and do not contain any group that can react with the textile fibre by means of a binder. They are commonly used in printing processes (pigment printing) (Nguyen, Chun Chieh, & Ruey, 2016). Organic pigments are largely benzoic derivatives and inorganic pigments (minerals) are derivatives of metals such as titanium, zinc, barium, lead, iron, molybdenum, antimony, zirconium, calcium, aluminium, magnesium, cadmium and chromium.

2.1.2. Impact of textile dyes on aquatic environment

The presence of textile dyes in wastewater discharged by textile industries in aquatic environments such as wades, rivers, seas, oceans... and the lack of their biodegradability, under normal ecological conditions can destroy the vital conditions of these different environments, while preventing the penetration of light to the depths of aquatic environments (Jieying, et al., 2017). As a result, there are serious ecological consequences such as changing the nature of aquatic environments and reducing photosynthesis compared to aquatic flora (Hosseini Koupaie, Moghaddam Alavi, & Hashemi, 2012).

In addition, these waste waters can produce several dangerous problems, namely aesthetic and health problems such as changes in the quality (colour and odour) of water and make it toxic, as they can cause allergies, dermatitis, skin irritations, cancers and mutations in humans (Hosseini Koupaie, Moghaddam Alavi, & Hashemi, 2012). Furthermore, between 60 and 70% of azo dyes are toxic, carcinogenic and are refractory to conventional treatment processes because of their resistance to conventional physicochemical destruction and the absence of

their biodegradability (Deepak, Vandana, Swagata, Lakhbeer Singh, & Radhey Shyam, 2018). This interrupted the phenomenon of photosynthesis in marine plants by triggering the phenomenon of eutrophication, under the effect of the release of mineral elements such as nitrates, nitrites and phosphates in an uncontrolled manner, and produced the long-term hazards of persistence, bioaccumulation, by products of chlorination, mutagenicity and carcinogenicity (Deepak, Vandana, Swagata, Lakhbeer Singh, & Radhey Shyam, 2018).

In addition, the existence of dyes and textile pigments in wastewaters makes them very characterized by a high degree of coloration, a very fluctuating pH and high levels in terms of biochemical oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC) and suspended solids (TSS) (Poon, Huang, & Fung, 1999). The uncontrolled increase in these pollution indicators can cause an imbalance in biological treatment plants because of the high toxicity of the metal elements contained in these dyes (metalliferous and pigments) (Zaroual, Azzi, Saib, & Chainet, 2006). As well as, the presence of mineral elements with very high levels in water and lack of their consumption by aquatic plants (algae, bryophytes, pteridophytes, spermatophytes and vascular plants) accelerates their uncontrolled proliferation in an uncontrolled manner and consequently leads to the oxygen depletion by inhibition of photosynthesis in the strata, deeper watercourses and stagnant waters (Hosseini Koupaie, Moghaddam Alavi, & Hashemi, 2012). This can affect the life of aquatic fauna and flora, modify the quality of drinking water production (Cardoso, et al., 2011).

In case of disposal of organic matter including dyes and pigments to the receiving media via textile finishing effluents, the natural processes of regulation can no longer compensate the bacterial oxygen consumption (Riera-Torres, Gutierrez-Bouzan, & Crespi, 2010). This may lead to under-oxygenation of stagnant aquatic environments, such that the degradation of 7–8 mg of organic matter by microorganisms is sufficient to consume the amount of oxygen in one litre of water (Sing Lai, Wan Loy, & Siew Moi, 2010).

2.2. Rice husks and their advantages

Rice is a major source of food in various countries of the world. Rice husk is the hard outer coating on grains of rice which protects the seed during the growing period. Around 20% of the total paddy weight is a husk, which is made of opaline silica and lignin(Ramezanianpour & Ramezanianpour, 2014)

The worldwide annual rice husk output is about 80 million tons and over 97% of the husk is generated in the developing countries(Silva, dos Santos, de Oliveira Machado, Tiago Filho, & Barros, 2021). Rice husk is an abundant agricultural waste that is generated at 545 million tons annually, which accounts about one fifth of the annual gross rice production of the world(Pode, 2016).

Rice husk can be recycled to produce high value eco materials, such as silicon (Si)(Marchal, Krug III, McDonnell, Sun, & Laine, 2015; Shen, 2017) , silica (SiO_2)(Araichimani et al., 2022), silicon carbide (SiC) (Araichimani et al., 2022), silicon nitride (Si_3N_4)(Moraes et al., 2014) and grapheme (G) (Zhang, Liou, Chiu, Hsu, & Liu, 2023). The chemical composition of raw rice husk has been reported to contain both organic 74% and inorganic constituents26% (Zou & Yang, 2019) . The organic constituents include cellulose, hemicellulose, lignin, L-arabinose, methyl glucuronic acid, d-galactose, proteins, and vitamins that can be removed from rice husks during the burning process(Datta & Halder, 2019) . The major inorganic component is Si_2O (80%), and the minor inorganic constituents include alumina (3.93%), sulphur trioxide (0.78%), iron oxide (0.41%), calcium oxide (3.48%), magnesium oxide (0.25%), sodium oxide (0.67%) and potassium oxide (1.45%)(Barnes, 2010) .

Chemical and physical properties of rice husks (G. Wu et al., 2015)

SiO2 (%)	Al2O2 (%)	Fe2O3 (%)	CaO (%)	K2O (%)	Na2O (%)	LOI (%)	MgO (%)	Specific gravity(g/cm^3)
0.10-1.23	-	-	-	0.10-2.54	0.01-1.58	5.90	0.01-1.96	-
87.86	0.30	0.93	1.30	2.37	0.12	-	0.35	-
94.60	0.36	0.40	0.70	2.54	0.07	2.10	0.30	2.10
86.98	0.84	0.30	0.40	1.30	0.20	2.05	0.30	2.05
87.30	0.15	0.90	0.86	1.67	0.12	3.13	0.31	-
90.70	0.40	0.73	1.40		2.46	5.14	0.57	2.10
94.50	0.21	0.16	0.55	3.68	1.12	8.55	0.35	2.06

Advantages of using rice husk derivatives as bio sorbent/adsorbent/sorbent are their biodegradability and good adsorption properties, which can be due to their morphology and surface functional groups. Their application has received much attention in sorption of various pollutants from aqueous media(Shamsollahi & Partovinia, 2019)

2.2.1. Adsorption capacity of rice husks

Rice husk derivatives as an adsorbent	Targeted metal ion	Experimental conditions	Adsorption capacity,qm(mg/g)	references
Rice husk ash	Fe(II)	Contact time;60min,concentration;2-40mg/L,Ph;5,temperature;30^0c,dose;0.6g	6.21	(G. Zhao, Wu, Tan, & Wang, 2010)
Rice husk ash	Mn(II)	Contact time;60min,concentration;2-40mg/L,PH;6,Temperature;300c,dose;0.6g	3.02	(Javier, 2014)
Activated carbon from rice husks	Pb(II)	Contact time;0-300min,concentration;50-500mg/L,PH;5,Temperature;300C	263.00	(Chen, Wang, & Zhang, 2021)
Rice straw	Cd(II)	Contact time;1440min,concentration;0.5-8.0mg/L,Ph;3,dose;0.2g	1.23	(Qu et al., 2020)
Rice husk ash	Cu(II)	Contact time;1440min,concentration;5-60mg/L,PH;3,Dose;0.2g	5.92	(G. Zhao et al., 2010)
Rice Straw	Cu(II)	Contact time;1440min,concentration;5-60mg/L,PH;3,Dose;0.2g	9.94	(Li, Gao, Li, & Yang, 2020)

2.2.2. Reported dyes adsorption capacities for rice husks.

Type of dye	capacity	researchers
Direct f scarlet	13.00	(Abdelwahab, El Nemr, El Sikaily, & Khaled, 2005)

Direct blue 67	37.92	(MOHAMAD ZU, 2013)
Direct red 31	57.88	(Abdelwahab et al., 2005)
Direct orange 26	43.00	(Safa & Bhatti, 2011)

2.2.3. Modification technique to enhance adsorption capacity of rice husks

Although rice husks is recognised to be an effective adsorbent for a wide range of solutes particularly water pollutants, they actually suffer from at least two major draw backs, which are low exchange of sorption capacity as well as poor physical stability (i.e. partial solubility)(Laszlo & Dintzis, 1994). This is due to the inert nature of polymer inside cellulose structure of rice husk. The polymer is relatively inert as the three hydroxyl groups of each cellulose unit responsible for most of the interactions with organic and inorganic substances are involved in extensive inter and intramolecular hydrogen bonding(Kumar, Sharma, & Singh, 2017). In addition, both lignin and silica constitutes a major obstacle in using rice husk as an adsorbent material. This is mainly because lignin acts as a cementing matrix between cellulose fibrils and hemicellulose molecules, while silica is present on the outer surface of rice husks in the form of silicon cellulose membrane(Ndazi, Karlsson, Tesha, & Nyahumwa, 2007). Lignin and silica can reduce the binding between accessible functional groups on rice husks surfaces and adsorbate ions/ molecules. Over and above, the inner surface of rice husk is smooth and contain wax and natural fats that provide good shelter for the grain but the presence of the impurities also affects the adsorption properties of rice husk chemically and physically(Chakraborty, Chowdhury, & Saha, 2011). Therefore, in order to overcome the associated problems, it is necessary for rice husk to be modified by several treatment to remove structural and compositional impediments to analysis and subsequent degradation processes in order to enhance digestibility, improve the rate of enzyme analysis, and increase yields of intended products(Tariq, Samsuri, Karam, Aris, & Jamilu, 2019). Moreover Wan Ngah and Hanafiah (2008) reported that, the treatments of rice husk can increase the cellulose content of the solid fraction by virtue of lignin removal and hemicellulose solubilisation. On top of that modification can also reduce cellulose crystallinity as well as increase adsorbent porosity nature. Accordingly, it has been determined that, the modification of rice husk can be done via three different routes of techniques, which are mechanical, physical and chemical treatment.

Mechanical treatment

According to (Paczkowski et al., 2021), the best mechanical performance is when the reduction of biomass below 20 mesh sieves. The purpose of mechanical treatment of rice husk are mainly for size reduction, as well as increasing digestibility of cellulose and hemicelluloses. In addition, mechanical treatment of rice husk can also increase specific surface area for solute surface interaction. This is due to the fact that, larger surface area will increase adsorption capacity at equilibrium. The table below shows types of mechanical treatment used in order to modify rice husk surface prior to using it as an adsorbent.

Table 9; mechanical treatment of rice husks

Type of mechanical treatment	**Mesh siever**	**references**
Crushing	**30**	**(Siddika et al., 2021)**
Grinding	**20-30**	**(Nugraha, Putri, & Matin, 2020)**
milling	**500-250**	**(Bogeshwaran, Kalaivani, Ashraf, Manikandan, & Prabhu, 2014)**

Physical treatment

The techniques of modification by physical treatment have been investigated intensively by previous researchers. It has been revealed that, elevated temperatures (i.e. pyrolysis, combustion, burning) are the most successful physical treatments in rice husk application as adsorbent. The physical treatment enables moisture loss as well as lignin decomposition of rice husk. On top of that, the treatment of rice husk by physical treatment also reduced the content of hemicellulose, lignin and cellulose crystallinity which leads to increase the specific surface area compared to raw rice husk.

Table 10; rice husk surface modification by physical treatment

Type of physical treatment	references
Heating up to;100^0C,120^0C,300^0C,350^0C,400^0C,500^0C,600^0C,750^0C	(Alvarez, Lopez, Amutio, Bilbao, & Olazar, 2015; Muthukrishnan, Gupta, & Kua,

	2019; Soltani, Bahrami, Pech-Canul, & González, 2015)
Burning at;650^{0}C(pyrolysis),400^{0}C	(Griffin, Ward, Madapusi, Shah, & Parthasarathy, 2022; Sirimirin, 2012)
Boiling For;30 min,30min+KOH	(Emdadi et al., 2014; Nayak, Nandi, & Datta, 2019; Song, Zhang, & Chang, 2012)

Chemical treatment

Chemical treatments of rice husks are able to reduce the content of hemicelluloses, lignin and cellulose crystallinity. The reduction in crystallinity leads to an increase in the specific surface area for treated rice husk compared to raw rice husk. Modification of rice husk by using powerful oxidizing agents such as ozone and hydrogen peroxide can effectively remove lignin; does not produce toxic residues; and the reactions are carried out at room temperature and pressure.

Table 11: types of chemical treatment used in order to modify rice husk prior to using it as adsorbent.

Type of chemical treatment	references
Acid; citric acid, methacrylic acid, sulphuric acid, nitric acid, hydrochloric acid	(Hokkanen & Sillanpää, 2020; Hsu et al., 2009; Hsu & Pan, 2007; Jiang, Wu, & Zhou, 2023; Kaur & Kaur, 2021; Kumari & Singh, 2018)
Alkali/base;	(abualnoun Ajeel, Sukkar, & Zedin, 2020; Halip et al., 2021; Harun & Geok, 2016; Jain, Rao,

potassium hydroxide, sodium hydroxide, ammonium hydroxide	Sambi, & Grover, 1994; Ndazi et al., 2007; Patel, Karera, & Prasanna, 1987)
Oxidising agents; hydrogen peroxide	(Bazargan, Wang, Barford, Saleem, & McKay, 2020; Z. Wang, Li, Barford, Hellgradt, & McKay, 2016)

2.3. Adsorption isotherms

Adsorption is a process in which a substance that is in a liquid phase accumulates on a s surface and is then removed from the liquid phase. An adsorption isotherm describes the equilibrium of adsorption of a substance on a surface at a constant temperature. It represents the amount of material bound to the surface as a function of the material present in the solution. In the adsorption process, the compound to be removed is called the adsorbate and the solid onto which the substance is adsorbed is called adsorbent(Awad et al., 2020; Majd, Kordzadeh-Kermani, Ghalandari, Askari, & Sillanpää, 2022). The adsorption isotherms are important for describing how the adsorbate molecules or ions interact with the surface adsorption sites. Therefore, correlation of the equilibrium data using a theoretical or empirical equation is essential for interpretation and prediction of adsorption(Bulut, Özacar, & Şengil, 2008). Several equilibrium models have been developed to describe the relationship of isotherms at equilibrium. The models used are those of Henry, Langmuir, Freudlich, Temkin, Dubinin-Radushkevich (DR), Redlich-Peterson (RP), Sips, Halsey, Harkin-Jura, Elovich, Flory-Huggins, Fowler-Guggenheim, Jovanovic, and kiselev(Busetty & Das, 2012; Daminescu et al., 2022).

2.3.1. Henrys isotherm

This isothermal model adequately describes the adsorption process at low concentrations so that all adsorbate molecules are without interaction with the neighbouring molecules(Al-Ghouti & Da'ana, 2020; Piccin, Cadaval, De Pinto, & Dotto, 2017). The concentrations in the phases are associated with a linear expression. It is expressed as;

$Qe=KH_ECe$ where qe is the adsorption capacity in equilibrium (mgg^{-1}); KH_E is the equilibrium constant of henrys; and Ce is the equilibrium concentration of the metal ions in the solution ($mg^{-}L$). From the straight line adjusted to graph Ce versus qe, the KHE coefficient was calculated, which is represented by the slope.

2.3.2. Langmuir isotherm model

The Langmuir equation assumes that the maximum adsorption corresponds to a monosaturated layer of adsorbate molecules on the surface of the adsorbent, the adsorption energy is constant, and there is no transmigration of the adsorbate on the surface of the adsorbent(Abin-Bazaine, Trujillo, & Olmos-Marquez, 2022). All adsorption sites are energetically identical, and the intermolecular forces decrease with increasing distance from the adsorption surface(Siddiqui, 2018). The Langmuir model is expressed by the following equation;

$Qe = \frac{qmKLCe}{[1+KLCeQe}]$ where qm is the maximum adsorption capacity ($mgg^{-}1$) and KL is the Langmuir constant ($Lmg^{-}1$)(Abbas, 2021). The linear form of the Langmuir model is;

$$\frac{Ce}{qe} = \frac{1}{qmCe} + \frac{1}{qmKL}$$

The value of the constants qm and KL are determined by the slope and intersection of the fitted line on the abscissa Ce and the ordinate$\frac{Ce}{qe}$, respectively. The characteristic of the Langmuir isotherm is that they can express a dimensionless constant called balance parameter or separation factor, which is expressed with the following equation

$$RL = \frac{1}{1 + (KL \times Ci)}$$

Where RL is the equilibrium parameter (dimensionless), and Ci is the initial concentration ($mgL^{-}1$). The RL values indicate what type of adsorption can be expected. RL>1 is unfavourable, RL=1 the adsorption is linear, RL=0 is irreversible, and if 0>RL<1, adsorption is favourable(Lata, Garg, & Gupta, 2008; Pandey, Sharma, & Sambi, 2010).

2.3.3. Freudlinch isotherm model.

The freudlinch model takes into account the heterogeneity of the surface of the adsorbent and an exponential distribution of the active sites and their energies. The freudlinch model is expressed by the following equation;

$Qe=KF+Ce_n$ where KF is the freudlinchs constant in (mgg^{-1}) and n is the freudlinch exponent related to the intensity of the adsorption; it is dimensionless. The equation of this model can be linearized as follows;

$$Logqe = \frac{1}{nlogCe} + logKF$$

The value of the constants KF and n are determined by the intercept and the slope of the graphical line on the ordinate Inqe and the abscissa InCe, respectively. The range of values of 1/n is between 0 and 1 showing the degree of non-linearity between the concentration of the solution and the adsorption. If the value of 1/n is equal to 1, the adsorption is linear(ILOKA, 2019). High levels of n indicate a relatively uniform surface, where low values mean high adsorption at low concentrations of solution. In addition, low values of n indicte the existence of high energy active sites(Mahmoodi, Taghizadeh, & Taghizadeh, 2018; Mall, Srivastava, Kumar, & Mishra, 2006).

2.3.4. Temkin isotherm model

The temkin isotherm model contains a factor that explicitly considers the adsorption interactions between the species and the adsorbate(Abin-Bazaine et al., 2022). The temkin model is described with the following equation;

$$Qe = BLn(KTCe)$$

Where $B=\frac{RT}{b}$, b is the temkin constant, KT is the Bound equilibrium constant (Lg^{-1}), and B is related to the heat of adsorption ($jmol^{-1}$)(Bensacia et al., 2014; E Al Prol, EA El-Metwally, & Amer, 2019). The temkin isotherm model is presented in linear form with the following equation;

$$Qe = BLne + BLnKT$$

To obtain the constants B and KT defined by the slope and intersection of lines, respectively, plot qe on the ordinate and LnCe on the abscissa.

2.4. Kinetic models

Various adsorption kinetic models, such as the pseudo-first-order (PFO) model (Lagergren, 1898), the pseudo-second-order (PSO) model(Hubbe, Azizian, & Douven, 2019), the mixed-

order (MO) model(Guo & Wang, 2019), the Ritchie's equation(Ritchie, 1977), the Elovich model(Ganguly, Sarkhel, & Das, 2020; Peers, 1965), and the phenomenological mass transfer models (Bouddour, Auriault, Mhamdi-Alaoui, & Bloch, 1998; Holubets, 2021; Powers, Abriola, Dunkin, & Weber Jr, 1994) have been developed to describe the adsorption kinetic process. However, some problems are existed in the applications of these kinetic models. The first one is that the most applied PFO and PSO models are empirical models and lack of specific physical meanings. We cannot investigate the mass transfer mechanisms by these empirical kinetic models(J. Wang & Guo, 2020).

2.4.1. First-order and pseudo first kinetic model

The Lagergren pseudo–first-order model is based on the assumption that the rate of change of solute uptake with time is directly proportional to difference in saturation concentration and the amount of solid uptake with time, which is generally applicable over the initial stage of an adsorption process(Crini, Peindy, Gimbert, & Robert, 2007). It is commonly observed that kinetics follows this Lagergren pseudo–first-order rate equation when adsorption occurs through diffusion through the interface.

The Lagergren pseudo–first-order model can be described by the following linear form:

$$\frac{dq_1}{dt} = K_1(q_e - q_t)$$

Where q_e and q_t (mg/g) are the amounts of the amount adsorbed at equilibrium and at time t, respectively; k_1 is the equilibrium rate constant in the pseudo–first-order model (L/min).

After integration and applying the boundary conditions, the following equation obtained:

$$\log(q_e - q_t) = \log(q_e) - \frac{K_1}{2.303}t$$

Value of k_1 is found from the linear plots of $\log(q_e - q_t)$ versus time.

If an adsorption process follows true first-order kinetics, then the intercept of $\log(q_e - q_t)$ versus t plots would be equal to log of experimentally determined q_e or adjusted to fit the experimental value. For slow adsorption process, true equilibrium can be difficultly reached, making it very difficult to measure q_e accurately.

Sometimes, the Lagergren pseudo–first-order equation does not fit well for the whole range of adsorption time. It is usually applicable over the initial 20–30 min of the adsorption process. It is then necessary to extrapolate the experimental data to infinite time to obtain q_e, which is often not possible. In this case, q_e is an adjustable parameter to be determined by trial and error.

In some cases(Yayayürük & Erdem Yayayürük, 2016), the pseudo–first-order equation is expressed as,

$$\frac{1}{q_t} = \frac{K_1}{Q_1}\Big/_t + \frac{1}{Q_1}$$

Where Q_1 is the equilibrium adsorption capacity (mg/g), q_t is the adsorption capacity at time t, and K_1 is the adsorption rate constant of pseudo–first-order adsorption (min^{-1}). If the adsorption process is in accordance with this equation, $1/q_t$ will show a perfect linear relationship with $1/t$.

2.4.2. Second-order and pseudo–second-order kinetic model

The pseudo–second-order kinetic model is based on the assumption that the rate-limiting step is chemical sorption or chemisorption and predicts the behaviour over the whole range of adsorption. In this condition, the adsorption rate is dependent on adsorption capacity not on concentration of adsorbate(Tanyildizi, 2011). One major advantage of this model over Lagergren first order is that the equilibrium adsorption capacity can be calculated from the model; therefore, there is theoretically no need to evaluate adsorption equilibrium capacity from experiment.

The differential equation for the pseudo–second-order kinetics is given by

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

After mathematical development, and taking into account the boundary conditions, the pseudo–second-order kinetic model is finally expressed as follows:

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

With

$$h = K_2 q_e^2$$

Where h is the initial sorption rate; q_e is the amount of the dye adsorbed at equilibrium (mg/g), and K_2 is the equilibrium rate constant of the pseudo–second-order model (g/mg min).

The plot of t/q_t as a function of time should give a linear relationship. From the slope $1/q_e$ and the intercept 1/h or $\frac{1}{K_2 q_e^2}$, we can calculate the amount of adsorbate adsorbed at equilibrium and gives K_2, the second-order rate coefficient.

2.4.3. Elovich kinetic model

The Elovich kinetic model is often used to interpret the kinetics of adsorption and successfully describe second-order kinetics assuming that the surface is energetically heterogeneous. It is given in the following equation(Rudzinski & Plazinski, 2009):

$$q_t = \frac{1}{\beta}(\alpha\beta) + \frac{1}{\beta} lnt$$

Where α is the initial adsorption rate and β is the desorption constant. By plotting ln t versus q_t, the constants can be obtained from the slope and intercept of the plot.

2.4.5. Weber and Morris kinetic model

To identify the diffusion mechanism in the adsorption, intraparticle mass transfer diffusion model has been proposed by Weber and Morris(F.-C. Wu, Tseng, & Juang, 2009). The equation may be written as follows:

$$q_t = K_i t^{0.5} + C_i$$

Where K_i is the intraparticle diffusion rate (mg/g $min^{-1/2}$).

If intraparticle diffusion is involved in the adsorption process, the plots of q_t as a function of $t^{0.5}$ should represent straight lines. The rate constants K_i and C_i (mg/g) are evaluated from the slope and intercept of the regression line. The values of C provide information about the thickness of the boundary layer. The larger C implies the greater effect of the boundary layer. However, nonlinearity is sometimes observed. This means that multiple processes are limiting the overall adsorption rate. In particular, if the data exhibit multilinear plots, this indicates that more than one process affected the adsorption. Therefore, these rate-limiting processes can be separated into different linear parts of the data over the time, in which they are exerting the control on the overall process(Robishaw, Berkich, & Neely, 1982).

2.5. Factors influencing kinetics and adsorption

The transfer of pollutants in aqueous media is governed by three physicochemical phenomena: the thermodynamic equilibrium between the two phases which expresses the limit of the process, the kinetics of adsorption, and the competition between the different dyes. Several factors will therefore influence these phenomena: particle size, adsorbent mass, initial concentration of the dye, pH, and temperature of the solution.

Initial dye concentration: Both for cationic and anionic dyes, the higher the dye concentration in the solution, the greater the adsorption capacity (amount of compound adsorbed per unit mass of adsorbent)(Aziz, Abdelmajid, Rachid, & Mohammadine, 2018; Salleh, Mahmoud, Karim, & Idris, 2011).

Adsorbent mass: For cationic dyes, the increased adsorbent mass implies a decrease in adsorbent capacity. This behaviour may be associated with the fact that as long as the amount of adsorbent added to the dye solution is small, the cations of the dye can easily access the adsorption sites; as it could be attributed to the fact that a large amount of adsorbent can create agglomerations of particles, resulting in a reduction in the total adsorption area and, therefore, a decrease in the amount of adsorbate per unit of adsorbent mass(Alene, Abate, & Habte, 2020). In the case of anionic dyes, the rise in the adsorbent mass leads to a reduction in the potential of adsorption. Owing to the increased amount of empty active sites on the adsorbent surface at a higher adsorbent dose, such a pattern could be predictable by the adsorbate molecules' number constancy(Wong et al., 2020).

Granulometry (the adsorbent particle size): this is a parameter closely linked to the specific adsorption surface area: Small particles have a large specific adsorption surface area and therefore perform much better than large particles(Wekoye, Wanyonyi, Wangila, & Tonui, 2020).

The pH of the solution: Anionic dyes are better adsorbed in acidic solutions while adsorption of cationic dyes is more effective in alkaline solutions(X. Zhao, Wang, & Lou, 2021).

The temperature of the solution: If the adsorption is favoured by low temperatures, it is exothermic, otherwise it is endothermic(H. Wang et al., 2021).

2.6. Limitations of using rice husks as an adsorbent

One of the main drawbacks to energy (electricity) generation from rice husks is their high ash content(Pode, 2016). Aside from the fact that the higher heating value of biomass is inversely proportional to its ash content(Bazargan, Bazargan, & McKay, 2015; Demirbas, 2002), the silica can form undesired deposits and slags during combustion, which can lead to operational problems(Míguez et al., 2021). The melting of the rice husk ashes (Armesto, Bahillo, Veijonen, Cabanillas, & Otero, 2002; Zareihassangheshlaghi et al., 2020) has been known to cause

agglomeration, fouling, and corrosion of heat transfer surfaces(Armesto et al., 2002; Surahmanto & Harnowo, 2020).

2.6.1. Application of rice husk

Unique physical and chemical properties of RH, like high ash content, silica content, it can be effectively used in domestic and industrial processing. Many of reports shown that, RH is used as fuel for different purpose, such as in brick kilns, in furnaces, in parboiling process of rice, the raw material for the production of sodium silicate, as an cleaning or polishing agent in metal and machine industry, briquettes molecular sieve(Babaso & Sharanagouda, 2017; Suwanvitaya, 1984).

As source of fuel. The calorific value of RH is 15217.20 KJ/Kg, efficiency of boiler found same as using of coal (68%) so RH is cheaper fuel than coal(Babaso & Sharanagouda, 2017);

As source of silica and silicon based materials; Due to high silica content of RH now, it became a source for a number of silicon compounds, silicon nitride, silicon tetrachloride, including silicon carbide, silica, zeolite, and pure silicon(ABDULHAMEED, 2016; Hossain, Mathur, & Roy, 2018).

As organic fertilizer; today, organic fertilizer plays important role in agriculture. RH is utilized as an organic fertilizer to improve not only productivity but also water use efficiency in field(Prasad, Shivay, & Kumar, 2017).

As source of pet food fibre and as source of dietary fibre; Traditionally, RH has been used as ingredient in ruminant and poultry(Fadaei & Salehifar, 2012). Rice husk has more than 30% dietary fibre, it is also an excellent source of protein and mineral, so it could use in food industry especially developing functional foods.

Used for making bricks (as building material); More porous and better thermal insulated brick can be made with high percentage of RH. Due to low thermal conductivity of air entrapped in pores, it makes porous fire brick structure suitable for back up insulation(Hwang & Huynh, 2015).

Preparation of activated carbon; The unique properties such as high surface area, large adsorption capacity and fast adsorption kinetics makes activated carbons as valuable material for different industrial applications. Production of activated carbon from rice husk is achieved

through activation with chemical or physical means(Liu et al., 2011; Menya, Olupot, Storz, Lubwama, & Kiros, 2018).

Used as silica source; The presence of silica in RH has been known since 1938 (Martin, 1938)(Bogeshwaran et al., 2014; Chandrasekhar, Satyanarayana, Pramada, Raghavan, & Gupta, 2003).

RHA have been used as fillers in polyethylene(Rahman, Islam, Huque, Hamdan, & Ahmed, 2010); In vulcanizing rubber(Da Costa, Visconte, Nunes, & Furtado, 2003); Manufacturing refractory bricks(Behera, Patra, & Mukharjee, 2023).

2.7. Challenges and future prospects

The future prospects of bio-adsorbents require researchers to face several challenges associated with these materials for proper use. One of these challenges is the search for potential feedstock materials and wastes as low-cost materials for the production process attaining good adsorptive properties.

2.8. Conclusions

In recent times, removal of dyes from aqueous solutions has captivated high attention owing to their adverse effects on the ecosystem and human health. Adsorption is a widely reported process for the removal of dyes and other organic pollutants from aqueous solutions due to its simplicity and effectiveness. As a result, several low-cost and natural materials have been utilized as precursors for the preparation of effective adsorbents.

CHAPTER THREE

3.1. Apparatus

Autoclave reactor, oven, digital analytical balance, thermally isolated magnetic stirrer, magnetic stirrer, volumetric flasks, electric grinder, conical flasks, measuring cylinders, beakers, pH meter, thermometer, stop watch, spatula, stirrer, soft cloth tissue, desiccator, centrifuge, aluminium foil, FTIR and UV-VIS spectrophotometer.

3.2. Materials

Thymolphthalein dye, potassium hydroxide, hydrochloric acid, distilled water, sodium hydroxide, sodium chloride.

Preparation of alkali solution of potassium hydroxide

The molar mass of potassium hydroxide was calculated in order to determine the required amount that was to be used;

Molarity=concentration (g/l)/RFM

Concentration =molarity×RFM

=1M×56.105g

=56.105g/l

56.105g/l were measured using a digital balance, distilled water was poured in a dry beaker and adjusted accordingly based on the calculated amount of potassium hydroxide. The calculated potassium hydroxide was then added into the beaker with continuous stirring to ensure complete dissolution. The solution was then transferred into a volumetric flask and filled up to the mark with distilled water. The flask was then sealed for use.

3.3. Preparation of the dye solution

Thymolphthalein, has a chemical formula $C_{28}H_{30}O_4$ of with molecular weight of 430.53g/mol.

1.0g of dye powder was dissolved in 1000ml of de-ionised water, respectively, to prepare the concentration of 1g/L dye solution. Solutions of different initial concentrations were prepared by dilution process of initial stock solution into 200mL of deionised water

3.4. Preparation of the adsorbent

Rice husks were collected from a local supplier in Nagongera and was thoroughly washed with distilled water to remove muddy materials. Then was soaked in sodium hydroxide to remove lignin-based colour materials and then washed with distilled water. The rice husks were then dried in an oven at 100^0C for 24hours to remove any excess moisture. After drying they were ground into fine powder using an electric grinder. Thermal treatment was carried out by burning rice husk using the autoclave Reactor. The rice husk was activated by potassium hydroxide in two different weight ratios; 1:1, 1:3 (rice husk ash: potassium hydroxide). The mixture was heated in the oven at a temperature of 180^0c for 24hours. After cooling, the sample was filtered and washed with distilled water to remove any residual alkali solution, oven dried at 100^0C for 24hours, then sieved to obtain uniform particle size. The sample was collected and neutralised with 0.5M hydrochloric acid and finally washed with distilled water.

Preparation of hydrochloric acid solution;

$C_1V_1=C_2V_2$

$11.8\times V_1=0.5\times 250$

$V_1=10.59$g of HCl

10.59g of HCL after weighing were transferred into a 1litre conical flask, and to it was added enough water to dissolve the HCl. The flask was filled to the mark with water, stoppered and the solution mixed well. The solution was then kept for use.

3.5. Characterisation of the adsorbent (FTIR analysis);

A small amount of activated rice husks was obtained and then ground into fine powder using a grinder, a potassium bromide pellet was then prepared by mixing a small amount of powdered activated rice husk with potassium bromide powder in the ratio of 1:100. The mixture was pressed using a pellet to form a transparent pellet which was then placed on a sample holder of the FTIR instrument. The FTIR spectra was then collected by scanning the sample in the desired wavelength range. The FTIR spectra was then analysed to identify the functional groups present in the activated rice husks sample.

3.6. Experimental procedure;

Adsorption studies;

3.6.1. Effect of contact time;

In a beaker was added a known volume of the dye solution (10ml) and to it was added a measured amount of the adsorbent (1g) ensuring proper mixing. The beaker was placed on a magnetic stirrer to ensure continuous mixing during the experiment. A stop watch was started and the rice husks were allowed to adsorb the dye for specific time intervals that is to say 30minutes, at a constant temperature.

After the desired time, the rice husks were separated from the dye solution by centrifuging such that the liquid is separated from the solid part.

The filtrate was collected for further analysis, the concentration of the dye in the collected filtrate was then measured using the uv-vis spectrophotometer.

And then a calibration curve was prepared using known concentrations of the dye to determine the concentration of the dye in the solution.

The amount of adsorbate adsorbed per unit mass of adsorbent was calculated using the following formula;

$$q = \frac{(Ci - Cf)}{m} \times V$$

Where q is the adsorption capacity (mg/g), Ci is the initial concentration of adsorbate (mg/L), Cf is the final concentration of the adsorbate (mg/L), V is the volume of the adsorbate solution (L), and m is the mass of the adsorbent (g).

3.6.2. Effect of initial dye concentration;

100ml of aqueous solution of thymolphthalein were diluted to make working solutions of different concentrations and to each concentration was added the same amount of adsorbent (0.5g), with time kept constant at 60 minutes and temperature also kept constant. The absorbance of each different concentration was measured using the uv-vis spectrophotometer.

3.6.3. Effect of amount of adsorbent;

10ml of aqueous solution of thymolphthalein were shaken for 90 minutes adding different amounts of adsorbents that is to say 0.2g, 0.4g, 0.6g and 1.0g and the absorbance of the filtrate was noted using a spectrophotometer at 590nm wavelength.

The absorbance of the filtrate was plotted against amount of adsorbent.

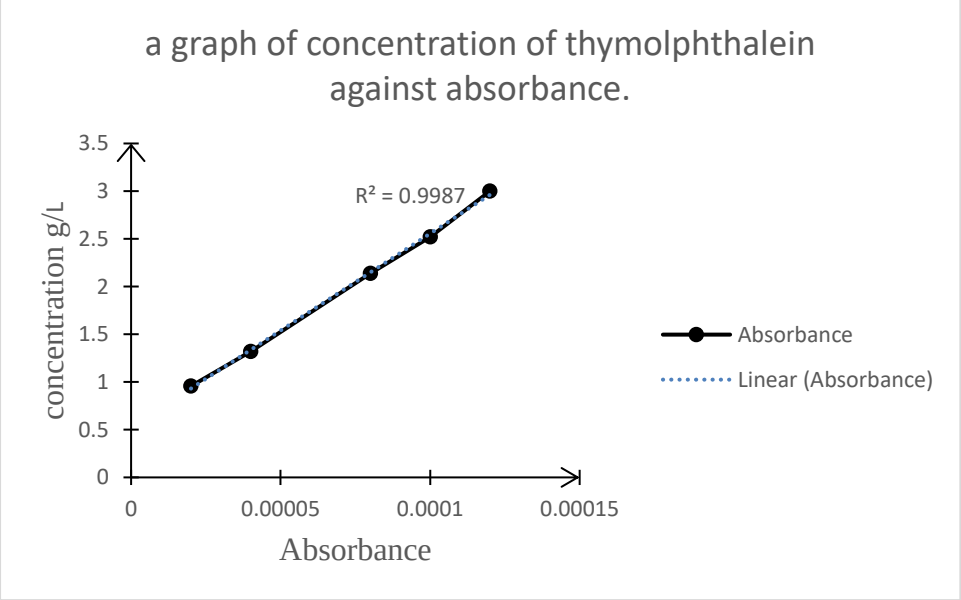
The experimental data were analysed using Langmuir and Freundlich isotherms.

CHAPTER FOUR; RESULTS AND DISCUSSION

4.1. RESULTS;

Calibration curve.

concentration/ g/L	Absorbance
0.00002	0.956
0.00004	1.32
0.00008	2.138
0.0001	2.521
0.00012	3



Effect of contact time

The percentage removal of thymolphthalein was calculated from;

%Q=$\frac{C_i - C_f}{C_i} \times 100$ Where Ci is the initial concentration of thymolphthalein; Cf is the final concentration of thymolphthalein

Results;

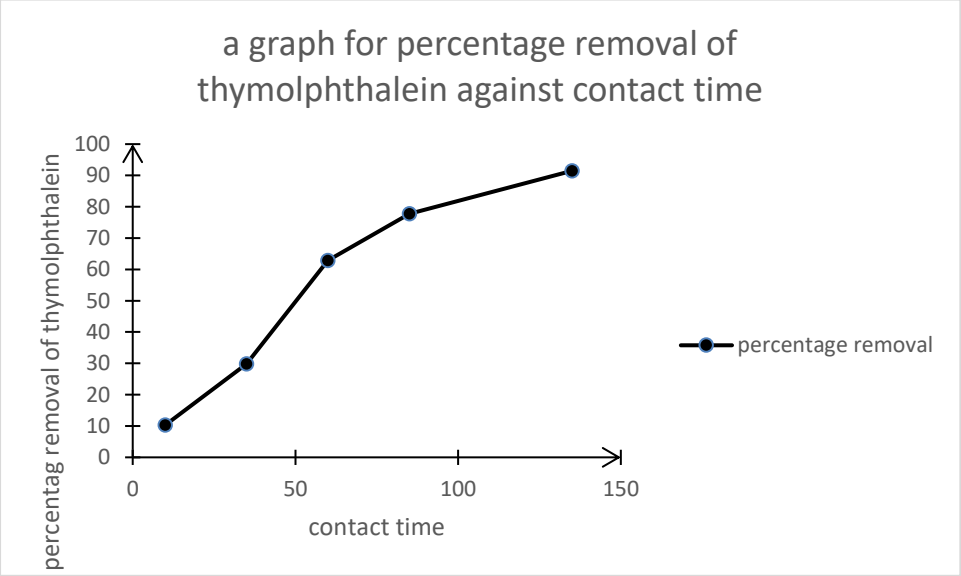
Amount of adsorbate=0.5g

pH of working solution=10.5

Initial absorbance=1.454

solution	Contact time (minutes)	Absorbance	Percentage removal
1	10	1.304	10.3
2	35	1.032	29.78
3	60	0.541	62.79
4	85	0.323	77.8
5	135	0.124	91.47

time	percentage removal
10	10.3
35	29.78
60	62.79
85	77.8
135	91.47



Effect of amount of adsorbent

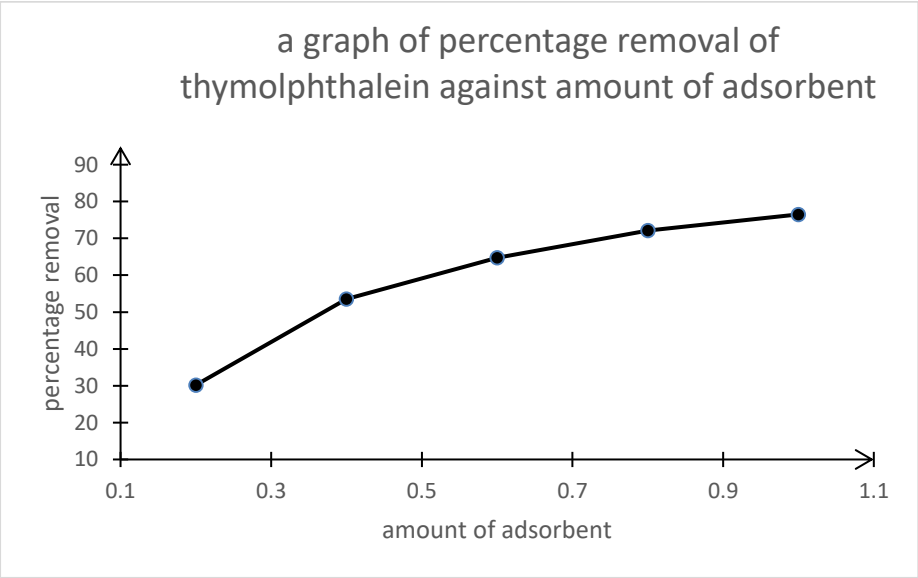
Contact time=60 minutes

pH of solution=10.5; temperature=room temperature

Initial absorbance=1.160

Amount of adsorbent	absorbance	Percentage removal
0.2	0.810	30.2
0.4	0.539	53.5
0.6	0.409	64.7
0.8	0.324	72.1
1.0	0.273	76.5

amount of adsorbent	percentage removal
0.2	30.2
0.4	53.5
0.6	64.7
0.8	72.1
1	76.5



Effect of initial dye concentration

PH of working dye solution=10.5

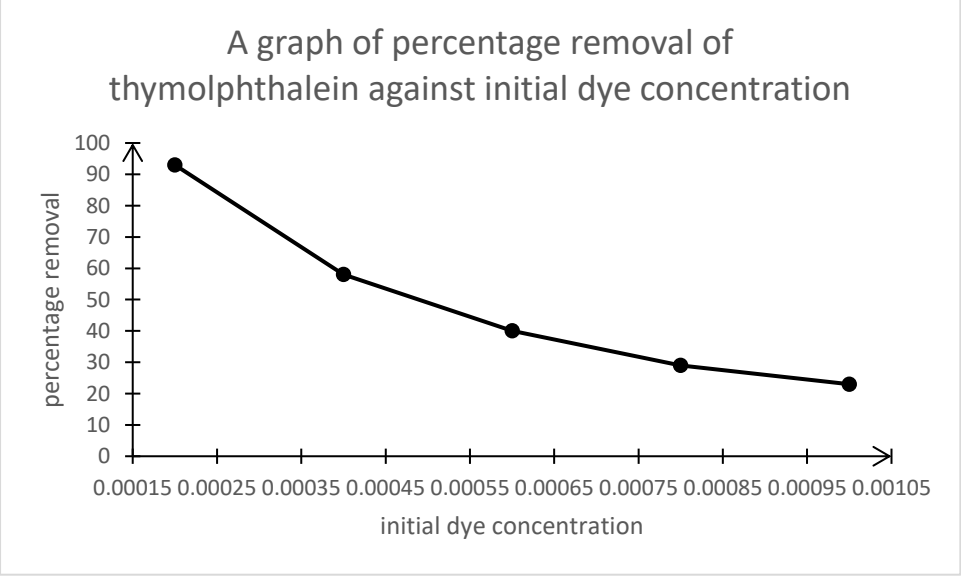
Amount of adsorbate=0.5g

Contact time=60 minutes

Initial absorbance=3.000

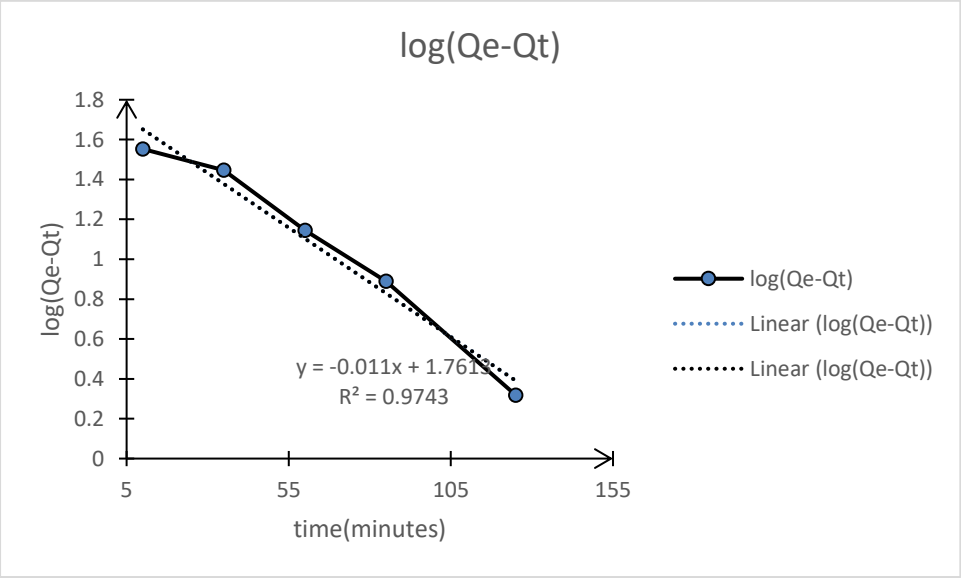
Initial dye concentration	absorbance	Percentage removal
0.0002	0.240	92
0.0004	1.260	58
0.0006	1.800	40
0.0008	2.130	29
0.0010	2.310	23

initial concentration	percentage removal
0.0002	92
0.0004	58
0.0006	40
0.0008	29
0.0010	23

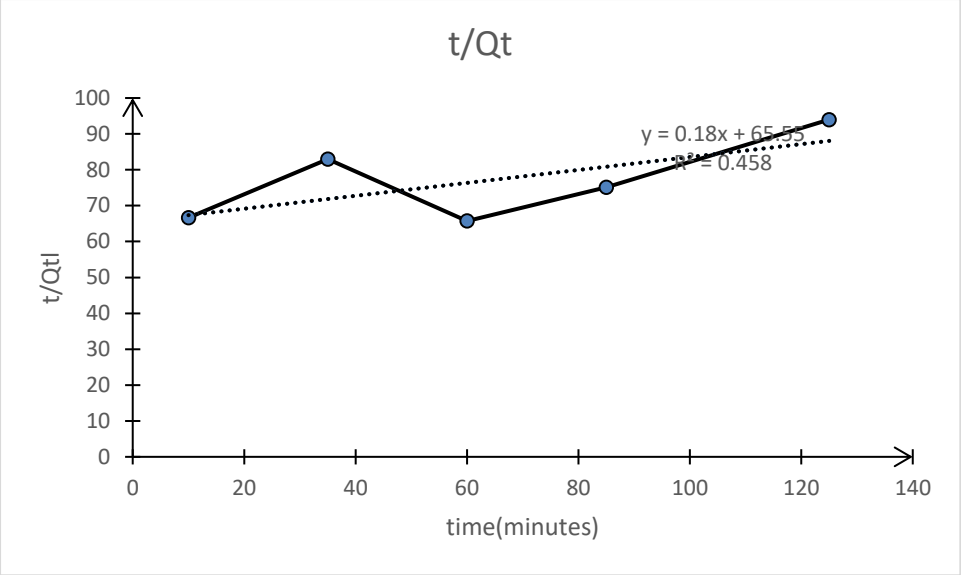


time	initial A	Final A	Qt	t/Qt	Ce	Qe	Ce/Qe	logCe	logQe	Qe-Qt	log(Qe-Qt)
10	1.454	1.304	0.15	66.667	17	35.873	0.474	1.230449	1.554768	35.723	1.552948
35	1.454	1.032	0.422	82.938	14	28.391	0.493	1.146128	1.453181	27.969	1.446677
60	1.454	0.541	0.913	65.717	7	14.883	0.47	0.845098	1.17269	13.97	1.145196
85	1.454	0.323	1.131	75.154	4	8.886	0.45	0.60206	0.948706	7.755	0.889582
125	1.454	0.124	1.33	93.985	1	3.411	0.293	0	0.532882	2.081	0.318272

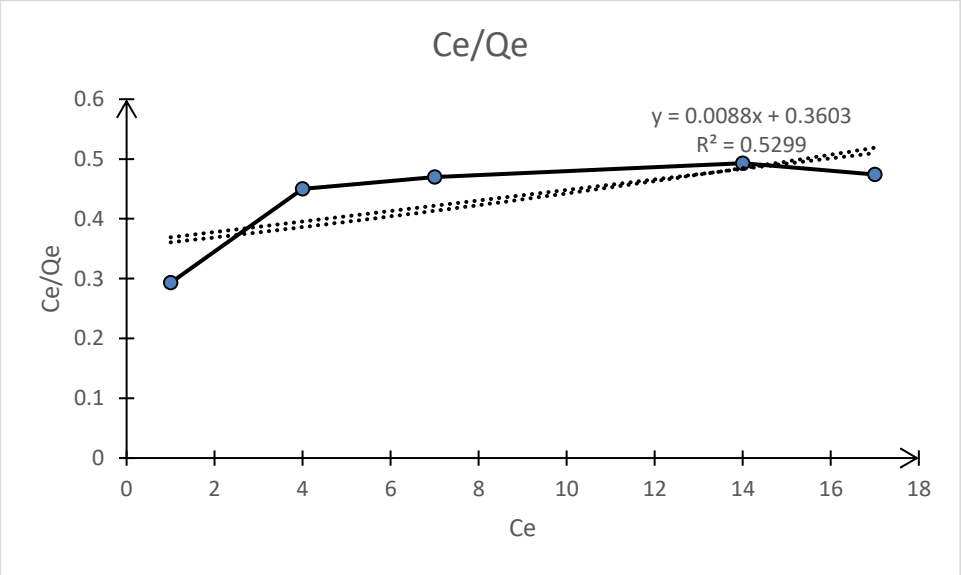
For first order kinetics;



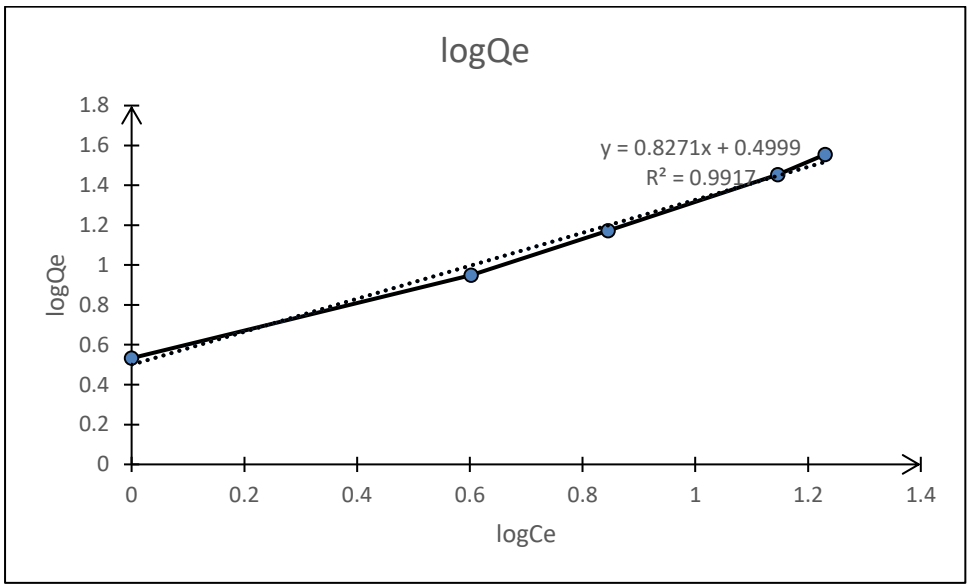
For second order;



For langmuir isotherm;



For freudlinch isotherm;



4.2. Discussion

4.2.1. Calibration curve;

As the concentration of rice husks increases, the absorbance also increased implying that the absorbance was directly proportional to the concentration of the absorbing species.

4.2.2. Effect of contact time;

Initially the percentage removal of thymolphthalein increased rapidly with increase in time and then became gradual up to a certain time where equilibrium was attained. The initial rapid increase in adsorption was because the surface of rice husks was clean with a high number of adsorption sites, as a result the thymolphthalein dye molecules occupied these sites quickly leading to a rapid adsorption.

As the contact time increased the adsorption rate became gradual and the system nearly approached equilibrium, a point where the rate of adsorption equals the rate of desorption. This is because the rice husk surface was fully saturated with thymolphthalein dye molecules and thus further increase in contact time did not result in significant additional adsorption.

Equilibrium was attained at around 150 minutes.

4.2.3. Effect of adsorbent dose;

The percentage removal of thymolphthalein increased with increase in the adsorbent dose. This was because more adsorption sites were available to bind with the thymolphthalein molecules.

However as the adsorbent dose was increased, a saturation point was reached where any increase in the adsorption dose has no significant effect on the adsorption of thymolphthalein.

The saturation point was at around 1.1g of activated rice husks.

4.2.4. Effect of initial dye concentration;

The percentage removal of thymolphthalein decreases with increase in dye concentration up to a certain concentration were equilibrium was attained.

Initially the percentage removal of thymolphthalein decreased with increase in concentration because the activated rice husks became saturated with thymolphthalein dye molecules quickly reducing their ability to adsorb more of them.

At a certain concentration of 0.00105ml of thymolphthalein, equilibrium was attained and thus no more dye molecules were significantly adsorbed. This is because the rate of adsorption was equal to the rate of desorption.

4.2.5. First pseudo kinetic order

The adsorption of thymolphthalein by activated rice husks follows first order kinetics. This is because the plot of log (Qe-Qt) against time is linear and gives a linear regression value which is approximately 1, 0.9743 R^2 value.

This implies that the adsorption of thymolphthalein by activated rice husks occurs on a mono layer.

4.2.6. Second pseudo kinetic model

The adsorption of thymolphthalein by activated rice husks does not follow the second pseudo kinetic model. Because the R^2 value is very small thus the plot is not perfect.

4.2.7. Freudlinch isotherm model

The adsorption of thymolphthalein by rice husks follows the freudlinch isotherm model rather than the Langmuir model because the R^2 value in freudlinch, 0.997 is more perfect than that in Langmuir model, 0.5299**.**

CHAPTER FIVE; CONCLUSION AND RECOMMENDATION

5.1. Conclusion

From the results and discussion above, it can be observed that rice husks are good adsorbents that can be used for adsorption and other purposes like waste water treatment. They are also abundant in occurrence since they can be applied as low cost effective adsorbents.

Also the adsorption of thymolphthalein follows the first pseudo order kinetics and the freudlinch isotherm model.

It is therefore important to investigate the adsorption capacities of various agricultural products which are available in our environments for the betterment of water treatment and finding cost effective methods of preserving water.

5.2. Recommendation

1. From the results obtained, more agricultural food products should be investigated about their adsorption capacities so as to come up with more cost effective water treatment methods.
2. Industries especially the textile industries should be cautioned on the effluents they release into the water streams that is to say guidelines that govern discharge of wastes in water bodies should be issued.
3. Relevant authorities should sensitize nitizens and industrial workers about the dangers of discharging a lot of colored waste in water streams.
4. More preaching about the knowledge of adsorption using low cost adsorbents should be done in order to develop more mechanisms of water treatment and dye manufacturing**.**

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