



Department of Process Engineering

Ref:...../U.M/F.S.T/2024

قسم هندسة الطرائق

رقم: / ج.م.ك.ع.ت//2024

MEMOIRE DE FIN D'ETUDES DE MASTER ACADEMIQUE

Filière : **GÉNIE DES PROCÉDÉS**

Option: **GÉNIE CHIMIQUE**

THÈME

Treatment of wastewater containing cationic dye using ZnS-Modified activated carbon: characterization, adsorption, and kinetic studies.

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Année Universitaire : 2023/2024

Acknowledgements

My heartfelt gratitude to Madam Dr Attouti MCA for accepting to be the President of the jury and Madam Dr Abdelli MCA for accepting to examine this work, it is equally an honour and a privilege and also would like to thank my supervisor Mr Termoul for his extraordinary aid in the redaction of this end of cycle project. His kindness, patience, availability and wisdom on even how to properly redact this end of cycle project. It is an honour and privilege to be under your supervision and I am extremely grateful for everything you have done for me Sir.

Would also like to thank all the PhD students especially Maiti Chaimaa who were all readily available and would always gladly help during the experimenting phase at the laboratory making the learning experience bearable and enjoyable, I am forever grateful. I would like to express also my heartfelt gratitude to my classmates with whom we would encourage each other at the laboratory, the teachers at the laboratory who treated me extraordinarily well, the chief of department who would always ask if everything was going well. My Zimbabwean family here in Mostaganem, my Azsa family and my beloved brothers at the residence who would sustain me in prayer and everyone else who contributed in the redaction of this work, thank you. Above all would like to thank God Almighty for it is only by his grace I managed in all.

Dedication

This work is dedicated to my lovely mother who has always been there for me, my father who taught me a lot and I still learn from him, all my beloved family and to all those who will find this writing useful in the bettering of humanity.

MANZVERA DESTINY

Abstract

The present study is focused on the adsorption of Rhodamine-B by nanoparticle-functionalized activated carbon (ZnS-NPs-AC). Activated carbon loaded with zinc sulphide nanoparticles was synthesized by a simple and cost-efficient method. This new material was characterized by FT-IR, XRD and pHzpc. The aim of this study was to evaluate the suitability and effectiveness of activated carbon loaded with zinc sulphide nanoparticles (ZnS-NPs-AC) for Rhodamine B adsorption. The adsorption study was carried out in batch mode and the parameters influencing adsorption, including pH, contact time and adsorbent dose, were optimized. In general, adsorption process parameters have a significant effect on percent removal. Adsorption was studied using three isotherm models, Langmuir, Freundlich and Temkin. The equilibrium data for Rhodamine-B removal follow strongly the Langmuir monolayer adsorption with a high adsorption capacity in a short time. The R^2 values were obtained with the Langmuir model is 0.86 for ZnS-NPs-Ac and 0.33 for Merck-AC. The adsorption capacity for ZnS-NPs-AC, q_{max} , was 86 mg/g at an initial pH of 3.57 and an equilibration time of 90 min at a temperature of 20 °C and an initial dye concentration of 50-500 mg/L and for Merck-AC is 106 mg/g. The kinetic study showed that Rh-B dye adsorption follows the pseudo-second-order kinetic model and intra particle diffusion. In addition, the adsorption mechanism of RhB-ZnS-NPs-AC is proposed, comprising three steps. The synthesized adsorbent is compared with other adsorbents in the literature, and indicates that the ZnS-NPs-AC nanocomposite used in this study showed good results at high physico-chemical characteristics compared with commercial activated carbon.

Keywords: ZnS nanoparticles, activated carbon, Rhodamine-B, Adsorption.

Résumé

Cette étude se concentre sur l'adsorption de la Rhodamine-B par du charbon actif fonctionnalisé avec des nanoparticules (ZnS-NPs-AC). Le charbon actif chargé de nanoparticules de sulfure de zinc a été synthétisé par une méthode simple et économique. Ce nouveau matériau a été caractérisé par FT-IR, XRD et pHzpc. L'objectif de cette étude était d'évaluer l'adéquation et l'efficacité du charbon actif chargé de nanoparticules de sulfure de zinc (ZnS-NPs-AC) pour l'adsorption de la Rhodamine B. L'étude d'adsorption a été réalisée en mode discontinu et les paramètres influençant l'adsorption, y compris le pH, le temps de contact et la dose d'adsorbant, ont été optimisés. En général, les paramètres du processus

d'adsorption ont un effet significatif sur le pourcentage de suppression. L'adsorption a été étudiée en utilisant trois modèles d'isothermes : Langmuir, Freundlich et Temkin. Les données d'équilibre pour l'élimination de la Rhodamine-B suivent fortement l'adsorption mono moléculaire de Langmuir avec une haute capacité d'adsorption en un court laps de temps. Les valeurs de R^2 obtenues avec le modèle de Langmuir sont de 0,86 pour ZnS-NPs-AC et de 0,33 pour Merck-AC. La capacité d'adsorption pour ZnS-NPs-AC, q_{max} , était de 86 mg/g à un pH initial de 3,57 et un temps d'équilibre de 90 min à une température de 20 °C et une concentration initiale de colorant de 50-500 mg/L, et pour Merck-AC, elle est de 106 mg/g. L'étude cinétique a montré que l'adsorption du colorant Rh-B suit le modèle cinétique du pseudo-second ordre et la diffusion intra particulaire. De plus, le mécanisme d'adsorption de RhB-ZnS-NPs-AC est proposé, comprenant trois étapes. L'adsorbant synthétisé est comparé à d'autres adsorbants de la littérature et indique que le nano composite ZnS-NPs-AC utilisé dans cette étude a montré de meilleurs résultats avec des caractéristiques physico-chimiques élevées par rapport au charbon actif commercial.

Mots-clés : nanoparticules de ZnS, charbon actif, Rhodamine-B, adsorption.

الملخص

ركزت هذه الدراسة على امتزاز رودامين-B باستخدام الكربون المنشط المفعّل بجسيمات نانوية من كبريتيد الزنك (ZnS-NPsAC). تم تصنيع الكربون المنشط المحمل بجسيمات نانوية من كبريتيد الزنك بواسطة طريقة بسيطة وفعالة من حيث التكلفة. تم تمييز هذه المادة الجديدة باستخدام FT-IR ، XRD ، pHzpc. كان الهدف من هذه الدراسة هو تقييم ملاءمة وفعالية الكربون المنشط المحمل بجسيمات نانوية من كبريتيد الزنك (ZnS-NPs-AC) في امتزاز رودامين-B. تم إجراء دراسة الامتزاز في وضع الدفعات وتم تحسين المعايير المؤثرة على الامتزاز، بما في ذلك الأس الهيدروجيني، وقت التلامس وجرعة المادة الممتزة. بشكل عام، تؤثر معايير عملية الامتزاز بشكل كبير على نسبة الإزالة. تم دراسة الامتزاز باستخدام ثلاثة نماذج توازن، وهي لانجمير، فريندليش وتيمكين. تبعت بيانات التوازن لإزالة رودامين-B بقوة امتزاز أحادي الطبقة لنموذج لانجمير مع سعة امتزاز عالية في وقت قصير. كانت قيم R^2 التي تم الحصول عليها مع نموذج لانجمير 0.86 لـ ZnS-NPs-AC و0.33 لـ Merck-AC كانت سعة الامتزاز لـ ZnS-NPs-AC ، q_{max} = 86 ملغ·غ⁻¹ عند أس هيدروجيني ابتدائي 3,57 ووقت توازن 90 دقيقة عند درجة حرارة 20 درجة مئوية وتركيز ابتدائي للصبغة 50-500 ملغ·ل⁻¹، وكانت لـ Merck-AC 106 ملغ·غ⁻¹. أظهرت الدراسة الحركية أن امتزاز صبغة Rh-B يتبع نموذج الحركية من الدرجة الثانية الزائفة والانتشار داخل الجزيئات. بالإضافة إلى ذلك، تم اقتراح آلية امتزاز RhB-ZnS-NPs-AC ، والتي تتكون من ثلاث مراحل. تمت مقارنة المادة الممتزة المصنعة بمواد ممتزة أخرى من الأدبيات، وأظهرت أن مركب NPs-AC ZnS- النانوي المستخدم في هذه الدراسة أظهر نتائج أفضل بخصائص فيزيائية كيميائية عالية مقارنة بالكربون المنشط التجاري.

الكلمات المفتاحية: جسيمات نانوية من ZnS ، كربون منشط، رودامين-B، امتزاز

List of Abbreviations

RhB: Rhodamine B

DNA: Deoxyribonucleic acid

AC: Activated carbon

CAG: Granular activated carbon

CAP: Powdered activated carbon

Merck-AC: Commercial activated carbon

ZnS-NPs-AC: Zinc sulphide nanoparticle activated carbon

Nps: Nanoparticles

pH: Potential hydrogen

pzc: Point of zero charge

FTIR: Fourier transform infrared

XRD: X-ray diffraction

cal: calculated

exp: experimental

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Introduction

A pollutant by definition is a substance which is a contaminant to a certain system with the systems being either the environment, human beings or animals. Dyes and pigments are among such pollutants which go on to pose a threat to some of the systems mentioned above as they are contributors to hazardous injuries to both animal and human health [1]. Dyes and pigments are present in wastewater, with manufacture (food, cosmetics, paper, and medicine industry) and textile industries being the major cause of this type of pollution. The textile industry uses large volumes of dyes with noted concentrations of 10-200 mg/L [2]. With the majority of these dyes being toxic, allergens and mutant. In terms of water bodies, such dyes go on to reduce both the appearance and quality of water. Also as an end result this goes on to cause skin and eye irritations, reduction of lung capacity, carcinogenesis and DNA linked behavioural disorders among people. An important statistic as of 2006, was noted that 10 000 various types of dyes were being used with also 700 000 tonnes of dyes are being used worldwide [3]. Most of these dyes in waste water are stable and in a non-biodegradable state and some even go on to limit the photosynthetic aspect of aquatic plants by the reduction of sunlight penetration [4].

Rhodamine B dye is a synthetic dye majorly used in the colouring in food and textile industries and it is a much commonly used pigment in various industries and also in areas such as the biological, analytical and optical sciences. Apart from its beneficial use in these different industries it has also proved to be hazardous to both aquatic and human life hence the need for its removal in waste water. When it comes to methods of separation for dye removal, methods such as: filtration, biological purification, coagulation, flocculation and chemical oxidations are already in place [4]. There is also separation by reverse osmosis on which membranes are applied. An important point to note is that these separation processes have certain disadvantages. For example coagulation and flocculation have reduced effectivity due to their low capacity to remove dyes from the wastewater and in operations where membranes are of use, the membranes in themselves are extremely expensive. In areas where a membrane is contaminated special treatment is required for their recovery [4], which might be costly in turn. Of the various methods adsorption is preferable due to its simple operation, high efficiency, production of high quality water [5] and less likelihood of causing secondary pollution. Adsorption by definition is a physical method in which natural or synthetic adsorbents are used to bleach or remove colourful compounds. For the provision of even much more effective results Nano adsorbents were put into place. Nano technology is an aspect which is crucial

and effective in science and also industry. It is of use as it helps to change the atom and molecular arrangement producing structures which were not in place before and due to their unique physical and chemical properties such as small size, high surface structure and high intra particle affinity they become ideal for cases of separation and adsorption. The formation of a Nano adsorbent is a procedure where nanoparticles are loaded on activated carbon (AC) which goes on to produce new and inexpensive adsorbents [6]. Examples of such nanoparticles which can be synthesized are zinc sulphide nanoparticles (ZnS), Zinc Oxide (ZnO) nanoparticles and even silver loaded nanoparticles.

This dissertation is divided into three major chapters: Chapter 1 which is pollution by dyes. How the pollution aspect takes place, why it is essential to depollute the polluted sources and lastly how Rhodamine B contributes in pollution, all these aspects are detailed in this chapter. Chapter 2 is majorly focused on the processes of adsorption and adsorbents. Where factors influencing adsorptions are detailed, the various adsorptions isotherms used for the result evaluation and the most common adsorbents used including their modifications is also detailed in this chapter. Chapter 3 which is the experimental part which is broken down into: Materials and Methods followed by Results and Discussion. This part includes results obtained for the adsorption of Rhodamine B by the commercial activated carbon and ZnS nanoparticles loaded on activated carbon.

The final part after the three chapters is then the general conclusion of the adsorption process and results obtained.

Chapter I - Pollution by dyes

Introduction

Dyes are pigments generally used in the different industries such as the textile industries and some go on to be used in the food industry. Though effective in their use in these different domains most dyes have proved to be extremely hazardous to both plant and animal life and due to this particular characteristic some have fallen into the category of being pollutants. Therefore giving need for their removal from textile wastes for instance before being discharged into water bodies.

I.1 Definition of pollution

Pollution by definition is simply the contamination of a system or environment by a substance which has the capacity to cause detrimental effects to either the system or entities inside the system upon its introduction. Such a substance which causes pollution is then termed a pollutant.

I.2 Definition of Rhodamine B

Rhodamine B, abbreviated as RhB with chemical formula $C_{28}H_{31}O_3N_3Cl$ is a reddish dye found in the Xanthene class. This class of dyes is among the oldest and most used synthetic dyes. These xanthene dyes tend to be fluorescent and they go on to give bright colours from pinkish yellow to bluish red [7]. Having a molecular weight of 479.029 g/mol, RhB exists in three monomeric molecular forms, cationic form, zwitterion form and lactone form.

I.3 Characteristics of Rhodamine B (RhB)

Rhodamine B is found to be a highly water soluble organic dye which is chemically stable and non-biodegradable [8]. With its part of non-biodegradability being attributed to its high molecular weight and its complex structure.

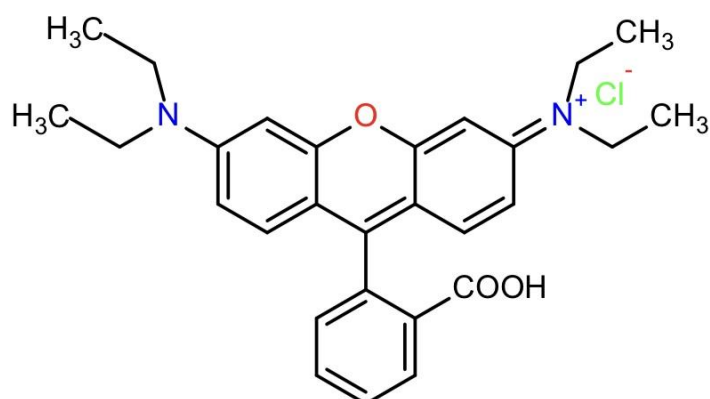


Figure 1. Structure of Rhodamine B [9]

Like others dyes RhB is found to be stable to light, heat and oxidation.

Table 1. Properties of Rhodamine B

Property	RhB
Chemical Formula	$C_{28}H_{31}O_3N_3Cl$
IUPAC name	[9-(2-carboxyphenyl)-6-diethylamino-3-xanthenylidene]-diethylammonium chloride
Class	Rhodamine
C.I name	Basic Violet 10
Suggested name	Rhodamine B
C.I number	45170
CAS number	81-88-9
λ_{max} (nm)	554
Solubility	5 g in 100 mL
Ionization	Basic
Molecular Weight	479.029 g/mol

I.4 Uses of Rhodamine B

Due the high solubility in water and basic low costs RhB is a commonly used pigment in various industries [9]. It is used as a colouring in the textile, paper and paint industry. RhB is extensively used also as a base for research studies due to its common use in the paper printing, textile and leather industry [10].

I.5 Toxicity and pollution

I.5.1 Toxicity

RhB has proved to be dangerous as when it does go on to enter the human body it causes various diseases especially liver cancer. Studies have also gone to show that it causes irritation and also redness and pain the eyes, vomiting, nausea and headaches. In the event of it being swallowed, RhB is likely to cause irritation to the gastrointestinal tract. In the case of inhalation it can cause irritation in the respiratory tract which will be seen with symptoms of coughs, a sore throat, laboured breathing and also chest pains [10]. RhB has also been discovered to cause subcutaneous tissue bone sarcoma and can form also equivocal tumour. In addition it has also been discovered to cause disruption of hormonal balance. It is also noted to be a toxic substance in trace quantities and seen also to be fatal in higher doses.

In terms of its toxicity to aquatic life, RhB has been proved to inhibit light penetration for aquatic life, leading to reduced photosynthesis activities. Experiments conducted have also shown that it is toxic to fish as certain fish species were found to be less in water polluted by RhB.

I.5.2 Pollution with dyes

The majority of the synthetic dyes are composed of aromatic organic compounds. These dyes go on to be classified into three categories which are anionic, cationic and non-ionic. In these three categories they can be further classified into basic dyes, and acidic dyes, reactive dyes and azo derivatives and these are some of the types of dyes generally used now in the textile industry and it is by their use in such industries such as the textile industry that they go on to contribute to pollution. As RhB is used in various industries, its then the mode in which it causes pollution through the improper discharge of waste water into water bodies thereby contaminating water bodies and also groundwater which goes on to pose a threat to plant or human life directly or indirectly. Natural water sources are then exposed to such pollutants through such improper disposals affecting also the production of sustainable drinking water mostly in developing countries.

Chapter II –Adsorption processes and adsorbents

Introduction

Adsorption is the most common method of separation used for depollution of contaminated substances especially in the area of water treatment containing pollutants from various industrial activities. Due to the dangers of the presence of the pollutants both to plant and animal life, their removal is found to be necessary with a low cost yet effective method. A criteria which the adsorption process meets fully well as high quality output water is collected on the removal of the dissolved organic compounds by the adsorption process.

II.1 Definition of adsorption

Adsorption is a process in which atoms of a body go on to attach to the surface of another body (the second body is usually a solid substance). The terms go on to be better defined by terming the solid on which adsorption takes place the adsorbent and the fluid which absorbs the adsorbate.

II.2 Adsorption types

There are two different types of adsorption which are physical adsorption and chemical adsorption. The difference between these two is mainly in the types of bonds formed and the energy used in the adsorption process.

II.2.1 Physical adsorption

This type of adsorption is also known as physio sorption. It requires low amount of energy between 5-40 kJ/mol and there is formation of bonds known as the Van Der Waals. These bonds formed are pertaining to the adsorbent and the molecule which would have been adsorbed. By reason of these weak bonds formed desorption is possible and can be achieved by an increase in temperature or decrease in pressure to achieve the desorption process.

II.2.2 Chemical adsorption

This type of adsorption also known as chemisorption, compared to physio sorption, this type requires high levels of energy above 40 kJ/mol. There is a formation of covalent bonds which are more permanent between the adsorbent and molecule absorbed. In chemisorption the

retention time is long and also the first layer linked to the surface of the adsorbent is chemically adsorbed. The other layers where they exist go on to be retained by physio sorption.

II.3 Adsorption Models

For the identification of the adsorption type and determination of the maximum capacity of the adsorbent, an adsorption model is used. There are different types of adsorption models such as the Langmuir model, Freundlich model, Temkin model and Sips model. These models also go on to show the interaction between the adsorbate and adsorbent. With the information obtained being further used for optimizing the use of an adsorbent.

II.3.1 Langmuir adsorption Model

The Langmuir model represents the equilibrium distribution of metal ions between the solid and liquid phases.

II.3.1.1 Langmuir model hypothesis

When the Langmuir model is confirmed appropriate for an adsorption process it suggests the below phenomena have taken place for that specific adsorption process:

- There are no interactions between the adsorbed molecules
- The adsorption process only takes place in monolayer
- The surface is uniform and all sites are equivalent
- Heat of the adsorption for each adsorption site is the same and is independent of the different fraction sites occupied by adsorbate

II.3.1.2 The Langmuir equation [11]:

$$q_e = \frac{Q_{max}^0 K_L C_e}{1 + K_L C_e} \quad (1)$$

q_e : the amount of adsorbate uptake at equilibrium in (mg/g).

C_e : adsorbate concentration at equilibrium in (mg/L).

Q_{max}^0 : maximum saturated monolayer adsorption capacity of the adsorbent in (mg/g).

K_L : the constant related to the affinity between adsorbent and adsorbate (L/mg).

II.3.2 Freundlich adsorption model

This model goes on to be applied for the quantification of the equilibrium relationship between the amount of adsorbate that will have been removed and the adsorbate concentration that will still be remaining in the solution.

It is easy to use for the description of the adsorption process on adsorption sites which would be energetically heterogeneous. The conditions in which it is applied is where there is a non-uniform distribution.

II.3.2.1 The Freundlich equation [11]:

$$q_e = K_F C_e^{1/n} \quad (2)$$

It can also be written in logarithmic form which is:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (3)$$

q_e : amount of adsorbate uptake at equilibrium in (mg/g).

K_F : Freundlich constant (mg/g).

n : Freundlich intensity parameter which has no dimensions.

C_e : adsorbate concentration at equilibrium in (mg/L).

II.3.3 The Temkin adsorption Model

This model should go on to show that the heat of adsorption should have a linear decrease with the adsorption coverage on an adsorbent. The conditions wherewith it is applied is in the case of a uniform distribution or a heterogeneous surface. This relation will be because of the interactions of adsorbate and adsorbent.

II.3.3.1 The Temkin equation [11]:

$$q_e = \frac{R_T}{b_T} \ln(k_t C_e) \quad (4)$$

q_e : amount of adsorbate uptake at equilibrium in (mg/g).

C_e : adsorbate concentration at equilibrium in (mg/L).

k_t : is the equilibrium binding energy in (L/g) corresponding to the optimum binding energy.

b_T : constant related to heat of adsorption (J/mol).

R is the ideal gas constant (J/mol K).

T : absolute temperature (K).

II.4 Factors influencing adsorption

For an effective adsorption to take place, the influence of factors such as the kinetic aspect for the adsorption, the nature of the adsorbent and adsorbate, temperature and the pH are taken into consideration.

II.4.1 Nature of adsorbent and adsorbate

The adsorbent will have different characteristics dependent on its phase, be it in the liquid phase or its gaseous phase. For the adsorbate, knowledge of its properties (physicochemical properties) is required, with its molecular structure being one of the major factors that affect the adsorption process. The more the molecular structure is volumetric, the more its retention by certain adsorbents is difficult and it is knowledge of such properties which help on the adsorbent choice.

II.4.2 Temperature

In terms of being endothermic or exothermic, the adsorption process can be one of the two, with the outcome solely dependant on the nature of the adsorbent and that of the adsorbate.

II.4.3 Adsorption kinetic

Knowledge of the adsorption kinetics helps in the area of optimisation. This is the area of the implementation of the optimality of the adsorbate and the factors that have to be optimised. Two models are used to examine the mechanism of diffusion in the adsorption process that would have occurred. These two models are the pseudo-first order model and the pseudo-second order model.

II.4.3.1 The pseudo-first order

This model also known as the Lagergren model and it goes on to consider the uptake of the adsorbate at a certain point in time to be directly proportional to the concentration difference and also the rate of adsorbate removal.

II.4.3.2 Equation for pseudo-first order [12]:

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t \quad (5)$$

II.4.3.3 Pseudo-Second Order

Kinetic data can be further analysed using the pseudo second order kinetic model. This model should go on to give a linear relationship after plotting of t/q_t against t .

II.4.3.4 Equation for pseudo-second order [12]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

q_e : amount of dye adsorbed at equilibrium in (mg/g).

q_t : amount of dye adsorbed at a given time (mg/g).

k_1 : pseudo first order constant in (min^{-1}).

k_2 : pseudo second order constant in ($\text{gmg}^{-1}\text{min}^{-1}$).

t : time (min).

II.4.3.5 Intra-particle diffusion model

Adsorption being a transport process of adsorbate molecules to the surface of the solid particles, this model the intra-particle diffusion model is then used to test the hypothesis that the transport of the adsorbate from solution to the adsorbate is the rate controlling state.

II.4.3.6 Equation for the Intra-particle diffusion model [12]:

$$q_t = K_{dif}^{1/2}t + C \quad (7)$$

q_t : amount of dye adsorbed at a given time (t) in (mg/g).

C: related to the lag phase where resistance to film diffusion has a contribution to the uptake kinetics (mg/g).

K_{dif} : intraparticle diffusion rate constant (mgmin/g)

t : time (min).

II.5 Adsorbents

When it comes to adsorbents, the commonly used adsorbent in the area of waste water treatment on a commercial scale is activated carbon (AC). This activated carbon is mostly found in the form of grain (CAG), powder (CAP) and sticks.



Figure 2. Activated carbon (CAP)

II.5.1 Sources and production of activated carbon

The common source from which activated carbon is produced from is coal but due to the unsustainability of coal other newer and renewables sources have been explored. Aside from coal, agricultural residues have been used as the needed raw materials in the production of the activated carbon (AC). Such agro based raw materials include rice husks which are the part left after the milling process of the rice grain, peanut shells cotton stalks and other

agricultural residues. Apart from mineral and plant origin activated carbon can also have animal origin. That is they can be obtained from animal bones. Though such raw products have to go through a process of carbonisation which is the first part where other impurities are removed at high temperatures and only the carbon is left. The second part after carbonisation is the activation of the carbon which is can either be physical activation or chemical activation. This activation process serves to increase the number of active sites necessary for adsorption and also increasing the volume of the pores.

II.6 Nano-adsorbents

II.6.1 Nanoparticles

Nano particles are simply particles of very small dimensions particularly in a range of 1-100 nm. These nanoparticles are generally in a spherical form therefore considered to be isotropic. They can also take other forms such as cubic forms, triangular form amongst others. Due to their various advantages their use their use has been adopted in various industries and areas such as communication and electronics where advantages such as the flexibility of electronic components are seen. Also in the transport department both air and road where we can go on to see an increase in engine efficiency amongst many other advantages and lastly also in adsorption processes.

II.6.2 Nanoparticles in adsorption processes

The use of nanoparticles in adsorption processes have been put in place due to the need by researchers for the increase of adsorption capacity , porosity and also the surface area of activated carbon. The introduction of nanoparticles into the activated carbon goes on to produce an adsorbent with enhanced adsorptive capacities. Various nanoparticles such as the silver (*Ag*)nanoparticles, zinc oxide(*ZnO*) nanoparticles, zinc sulphide (*ZnS*) amongst many types of nanoparticles used.

II.6.3 Advantages of Nanoparticles in Adsorption

- Simple and also low cost of synthesis
- A small amount of nanoparticles is needed to for the adsorption process
- They have a high adsorption capacity due to their high specific area and availability of a larger quantity of unsaturated atoms
- Other nanoparticles like zinc oxide have photocatalytic and antibacterial properties
- Most are non-toxic and also have been found to be thermally stable

II.6.4 ZnS nanoparticles

Zinc Sulphide (ZnS) is a transparent semiconductor which has been found to be of use in various areas, adsorption included. ZnS is a semiconductor of type II-VI, which implies that it is comprised of an element from group II and VI of the Mendeleiev periodic table. With the Zn belonging group II and Sulphur belonging group VI. From a structural point of view, ZnS is known to have two crystalline phases [13]. The first is cubic zinc blende structure called also sphalerite followed by the hexagonal wurtzite structure.

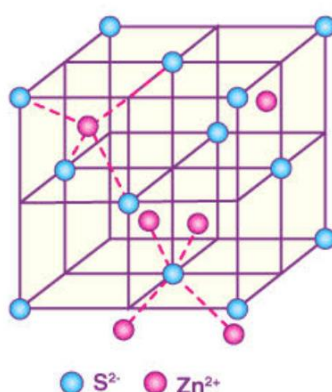


Figure 3. ZnS cubic structure

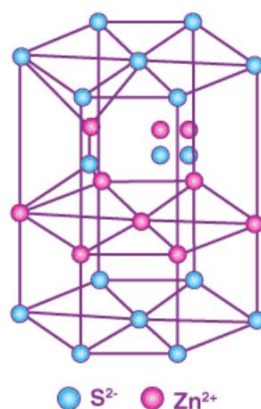


Figure 4. ZnS wurtzite structure

In this thesis ZnS nanoparticles loaded on activated carbon have been used also in parallel with commercial activated carbon for the removal of the pollutant RhB.

II.6.5 Applications of ZnS nanoparticles

Zinc Sulphide can also be used in a wide range of applications such as in optical sensors, catalysts and biomedical detection [14].

II.6.6 Advantages of ZnS

- It is not toxic for the environment
- It has a high refractive index
- A high binding energy

It also has some disadvantages as noted belows.

II.6.7 Disadvantages of ZnS

- Point defects caused by vacancies and foreign atoms
- Linear defects caused by sub grain boundaries and dislocations

Chapter III - Experimental part

Introduction

In every scientific study the experimental process is equally important as the theoretical process. This is because the suggested hypothesis have to be tested to prove both their effectivity as compared to the already existing standard results and also the conditions in which they are most effective. This Chapter is comprised of detailed results of the experimental process of the removal Rhodamine B dye using both the commercial activated carbon and ZnS nanoparticles loaded on activated carbon and also the conclusion reached after analysis of the results obtained.

III.1 Materials and Methods

III.1.1 Materials

- Activated commercial Carbon
- Zinc Acetate
- Sodium Sulphate Na_2S
- Solvents: distilled water and ethanol
- Equipment: high temperature muffle furnace, magnetic stirrer, beakers, filters, analytical balance

III.1.2 Preparation protocol

III.1.2.1 Preparation of ZnS nanoparticles

Dissolution of zinc acetate: dissolving an appropriate amount of zinc acetate in 150 mL of distilled water under magnetic stirring to obtain Zn^{2+} solution of a known concentration.

III.1.2.2 Preparation of sodium sulphate Na_2S

Dissolve the appropriate amount of Na_2S in 150 mL of distilled water with magnetic stirring to obtain a solution of S^{2-} solution of known concentration.

III.1.3 Preparation of ZnS-NPs-AC

Weigh 5 g of commercial activated carbon which has been washed and dried at temperature 110 °C overnight and mix it with 150 mL of the Na_2S solution with magnetic stirring. Continue stirring until a homogeneous suspension is obtained. Slowly add the Zn^{2+} solution to the activated carbon suspension with constant stirring. Then allow the dispersion to

stabilise for 30 minutes. This will cause the ZnS nanoparticles to precipitate directly on the activated carbon surface. Continue stirring for up to 2 hours to ensure homogenous distribution of the nanoparticles. Filter the mixture to separate the activated carbon ZnS nanocomposite. Wash the precipitate with distilled water and ethanol to remove the residual ions. Dry the suspension obtained to remove the solvent. This can be done by evaporation of followed by drying in oven at 105 °C overnight. Place the dried material in a crucible and heat it in a high temperature oven. Heat gradually until reaching 650 °C and maintain this temperature for 3 hours to allow formation and deposition of ZnS nanoparticle on activated carbon. Allow the composite to cool naturally to room temperature inside the oven before removing it. Washed with lukewarm water and then dried in the oven at 65 °C finally the nanocomposite is ready for use.

III.2 Characterisation

Adsorption spectra measurements on the ZnS nanoparticles loaded on activated carbon were conducted these include Fourier transform infrared (FTIR) analysis, pH point of zero charge (pH_{pzc}), X-ray diffraction (XRD) analysis and Iodine number determination.

III.2.1 Fourier transform infrared (FTIR) analysis

This analysis is used in the determination the various functional groups present in a substance [15]. An FTIR spectrometer is used for this determination.

III.2.2 Point of zero charge pH_{pzc}

The determination of this point is obtained by the fixing of different pH values of the same solution from a given pH range. With a specific mass of the nanoparticle loaded on the activated carbon being added to the different pH solutions it is left sealed and shaken for a period of 24-72 hrs. After this time interval difference the final pH is determined and plot of the difference in pH the final and the initial against the initial pH is done [15].The pH_{pzc} is obtained graphically as it is the point where the plotted line cuts the x-axis.

III.2.2.1 Protocol for point of zero charge determination

Six measurements of 0.15 g of the ZnS-NPs-AC were done and to each was added 50 mL of 0.01 M NaCl solution of different pH values ranging from 2 to 12. The pH was adjusted by the addition of HCL or NaOH solution. These six samples were kept in constant stirring at room temperature for 48 hrs and the final pH was measured after this duration of time for each sample.

This same procedure for the Merck-AC so as to obtain its pH_{pzc}.

III.2.3 X-ray diffraction (XRD) analysis

The XRD analysis serves to investigate the material structure of the nanoparticle activated carbon [15].

III.2.4 Iodine number determination

The iodine number is a relevant parameter to be measured as it is used in analysing of the carbon performance. The iodine number is simply a measurement of the carbon content through the adsorption by iodine molecules [15]. The determination of this number goes on to help as it can also be applied in the determination of porosity, the total surface area of the nanoparticle activated carbon.

For the determination of the iodine number, solutions of hydrochloric acid, 0.1 N iodine and sodium sulphate at concentration 0.1 N are first prepared.

III.2.4.1 Preparation of solutions

To prepare an iodine solution with a concentration of 0.1 N weigh 30 g of crystallized potassium iodide and dissolve it in the lowest possible quantity of water. Afterwards 12.69 g of sublimated iodine is weighed and added to the potassium iodide found in a 1 L volumetric flask and the solution is shaken with the volumetric flask being closed. Until the iodine dissolves then fill up the volumetric flask with distilled up to the 1 L mark of the volumetric flask and the solution is placed away from sunlight penetration.

To prepare a solution of sodium thiosulfate with a concentration of 0.1 N, 24.82 g of this salt is introduced into 1 L volumetric flask and a small quantity of distilled water for the dissolution of the salt is added to the volumetric flask after dissolution of the salt, fill up the 1 L volumetric flask to the mark with distilled water.

III.2.4.2 Procedure for determination of iodine number

For the determination of the iodine number for each activated carbon, three solutions are required: a solution of hydrochloric acid (HCL) with a concentration of 5 % (v/v), 0.1 N iodine solution and a solution of sodium thiosulfate with a concentration of 0.1 N.

Weigh 0.6 g of the sample dried activated carbon sample which had been previously dried at 150 °C in the oven for 3 hrs and introduce this sample into a bottle. Add 10 mL of HCL to the measured sample and stir gently until the sample is completely wet, boil the sample for 30 s, allow to cool to room temperature. Introduce 100 mL of iodine solution into the bottle,

cap immediately and stir for 30 s, thoroughly filter then discard the 20 to 30 mL of the filtrate and collect the rest in a beaker. Pipette 50 mL into a clean 250 mL Erlenmeyer flask, titrate with sodium thiosulfate until the solution turns pale yellow. Add 2 mL of freshly prepared starch or thiodene and titrate dropwise until the colour of the solution turns transparent. Note the volume V' at this point and finally calculate the molarity of the filtrate R from the below equation:

$$R = \frac{0.001 \times V'}{2} \quad 8$$

To calculate the correlation factor (D) by application of the below equation:

$$D = \left(\frac{0.01}{R} \right)^{0.165} \quad 9$$

To calculate the iodine index the below equation is used:

$$\text{Iodine number (mg/g)} = \frac{[1269.1 - (V' \times 27.92)] \times D}{m} \quad 10$$

D : correlation factor.

R : molarity of the filtrate.

V' : volume of sodium thiosulfate.

III.2.5 Adsorption batch tests

For the optimisation of the adsorptions parameters, batch adsorption tests such as effect of dose time and pH were done. The objective of the batch adsorption tests was to find the optimal conditions at which the adsorption process is more effective.

III.2.5.1 Effect of time

To investigate the effect of time on the adsorption process a quantity of 0.1 g was measured for both the ZnS-NPS-AC. This same mass was measured for seven different samples for the ZnS -NPs-AC. 25 mL of RhB solution was added to the various samples of the ZnS-NPs-AC over a range of time of 5 to 180 mins and left at constant stirring on a magnetic stirrer at room temperature with each sample having a specific time at which it is in contact with the dye.

The study involved starting with the sample at 180 mins and gradually adding other samples in decreasing order. This was done so as to ensure that no sample will exceed the allocated contact time leading to erroneous results. The solutions after the adsorption process were separated using a centrifuge for 15 mins and the absorbance values measured using a spectrometer.

The same procedure was done also for the Merck-AC.

III.2.5.2 Effect of dose

After the studying the effect of contact time and obtaining an optimal time, the effect of dose on the adsorption process has to be investigated. Six samples of 0.025 g, 0.05 g, 0.1 g, 0.15 g, 0.2 g, and 0.25 g of ZnS-NPs-AC were measured. 25 mL of RhB solution was added to each sample and all samples were left to stir on a magnetic stirrer at room temperature for the same amount of time which would be the optimal time obtained for the contact time effect. With the adsorption process being achieved at the optimal time the sample solutions are placed and the centrifuge for 15 mins for separation of the adsorbent and the adsorbate. The absorbance value for each sample is then measured.

The same procedure is repeated with the Merck-AC to study its dosage effect

III.2.5.3 Effect of pH

After having established the optimal time and optimal dose experimentally, another parameter to study is the pH effect as adsorbents performance differ at different pH and the aim of this study of pH effect is to find the optimal pH at which the adsorbent performs exceedingly well.

With the optimal time, the optimal dose obtained, the pH is varied from a range of 2-12. The adjustment of pH is done by either the addition of NaOH or HCL. Through the adjusting of the pH, six samples with different pH values in the range of 2-12 are obtained and using the optimal values for time and dose effect, the six samples are left to stir on a magnetic stirrer room temperature. After the adsorption process separation of the adsorbate and adsorbent in the various samples is done by the use of a centrifuge for a time of 15 mins and the absorbance values are measured using the spectrometer.

This procedure is done both for the ZnS-NPs-AC and the Merck-AC.

III.2.6 Kinetic adsorption

With the contact time, the dose and pH optimised, two solutions of the RhB solutions of concentrations 200 mg/L and 300mg/L are used to study the adsorption kinetics for the ZnS-NPs-AC and the Merck-AC.

25 mL of the 200 mg/L solution at optimal pH is added to various samples of ZnS-NPs-AC containing the optimal dose. The contact time for the different samples is varied between 5 min and a bit beyond the optimal time for confirmation of the results obtained.

The same procedure is done for the Merck-AC using the 200 mg/L RhB solution and also for the study of adsorption kinetic for the 300mg/L RhB solution, the same procedure is done also for both the Merck-AC and the ZnS-NPs-AC.

III.3 Results and discussion

III.3.1 Characterisation of ZnS

III.3.1.1 Fourier transform infrared (FTIR) analysis

The Fourier transform infrared analysis was studied and by the analysis of the spectra obtained, deduction of the functional groups present on the surface of both the activated carbon used made.

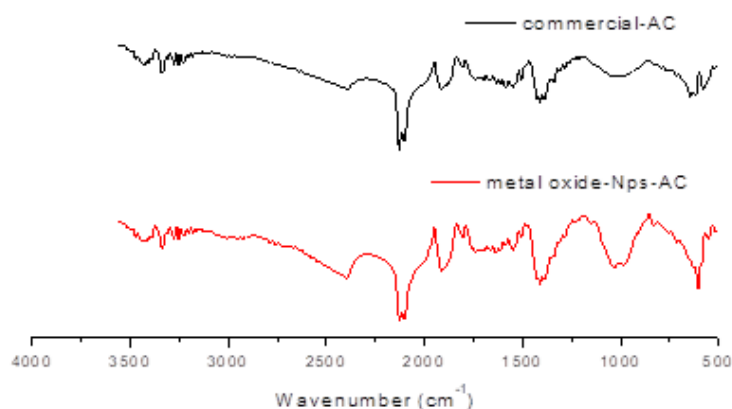


Figure 5. FTIR spectrum for ZnS-NPs-AC and Commercial AC

For both the ZnS-NPs-AC and Merck-AC the form of the peaks was relatively the same from a wavenumber of 3600 cm^{-1} to 2500 cm^{-1} , with both activated carbons also having intense peaks at a wavelength of 2200 cm^{-1} . From the wavelength of $2000\text{--}500\text{ cm}^{-1}$, ZnS-NPs-AC was noted to have sharper peaks than the Merck AC with all the peaks in this given wavelength range being less intense than the peak obtained at 2200 cm^{-1} for both activated carbons.

Generally for the Merck activated carbon it is found at peaks of between $750\text{--}1746\text{ cm}^{-1}$ and results obtained are close to that range for the Merck-AC. For the ZnS-NPs-AC it is generally found at peaks of around 1100 cm^{-1} , 900 cm^{-1} and 600 cm^{-1} .

III.3.1.2 X-ray diffraction (XRD) analysis

For the investigation of the material structure of the Merck-AC, the below spectra for the XRD analysis was obtained.

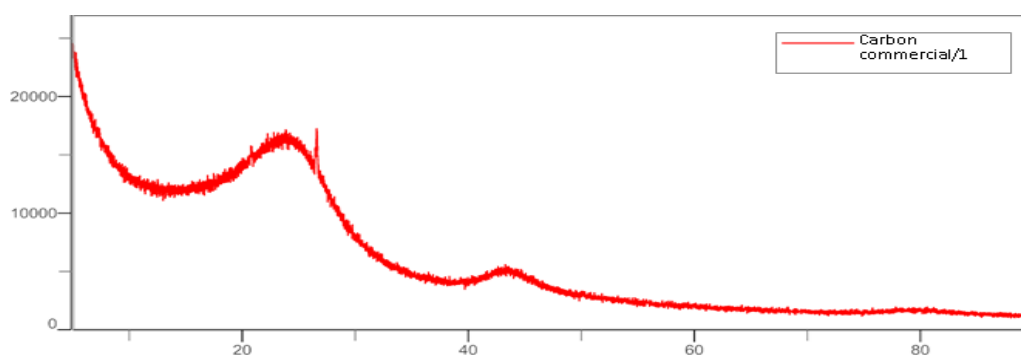


Figure 6. XRD analysis for Commercial- AC

The spectra shows two broad diffraction peaks obtained at around 23 °C and 43 °C for the Merck-AC. These peaks correspond to the 002 and 100 diffraction planes of graphite with the first peak being a 100 peak characterised by a broad diffraction peak and the second peak being a 002 peak characterised by a narrow diffraction peak.

The diffraction peak obtained at 23 °C confirms the amorphous nature of the Merck-AC which according to normal standards is confirmed by a peak at 24°C.

The XRD analysis for ZnS-NPs-AC carbon was also studied and the XRD profile obtained is shown below:

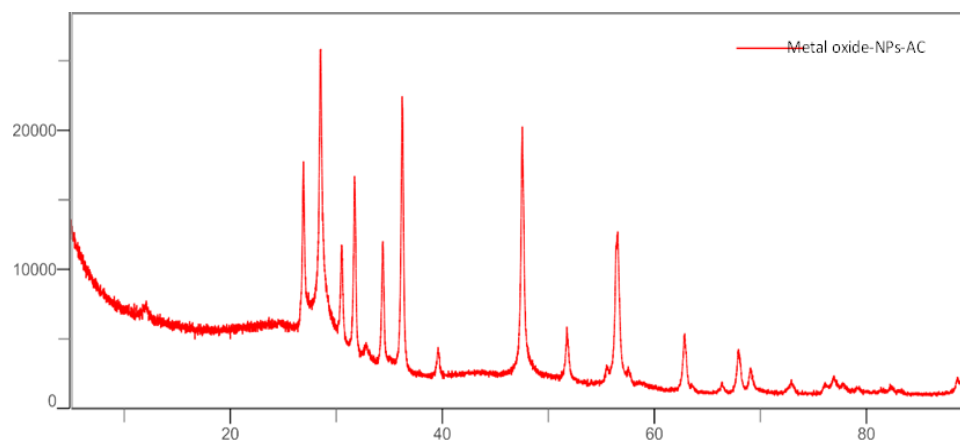


Figure 7. XRD analysis for ZnS-NPs -AC

Figure 7 shows that various sharp peaks were obtained over the range of temperature from 29-70 °C, with the largest peak being noted to be at a temperature of 24 °C. This peaks confirms the amorphous nature of the ZnS-NPs-AC as it corresponds to the general peak of Merck-AC which confirms amorphous nature of the activated carbon in study.

III.3.1.3 Point of zero charge pH_{pzc}

The pH_{pzc} is described as the pH at which there is absence of charge be it negative charge or positive charge at the surface of the activated carbon.

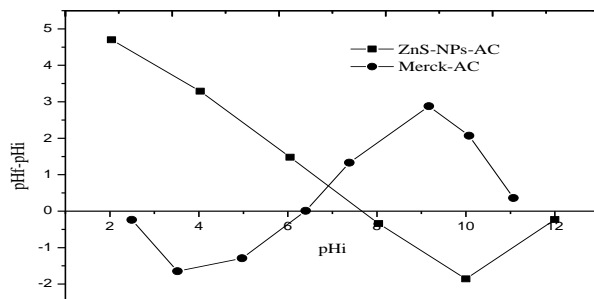


Figure 8. pH_{pzc} for ZnS-NPs-AC and Commercial Activated Carbon

The pH_{pzc} for the commercial AC and ZnS NPs AC was found to be 6.3 and 7.8 respectively for the two activated carbons. The pH_{pzc} of the Merck-AC after modification by ZnS nanoparticles increased from 6.3 to 7.8 due to the addition of alkaline functional groups on the surface of the activated carbon. At $\text{pH} > \text{pH}_{\text{pzc}}$ an attraction between the positively charged Zn^{2+} and the negatively charged surface of the activated carbons causing an increase in adsorption capacity. At $\text{pH} < \text{pH}_{\text{pzc}}$ repulsion occurs [16] as both the Zn^{2+} and the surface of the activated carbon are positively charged leading to a decrease in adsorption capacity.

III.3.2 Adsorption Tests

To prove the adsorption effectivity of the ZnS-NPs-AC, various experiments were carried out whereby the effect of parameters such as contact time, dosage, adsorption kinetic on the ZnS-NPs-AC were studied. The results obtained from these experiments became the basis by which a conclusion could be made on the effectivity of the ZnS-NPs-AC.

III.3.2.1 Effect of contact time

The equilibrium time is one of the most important factor to consider in wastewater treatment. RhB adsorption was studied as a function of contact time so as to determine the equilibrium time. A graph of the removal percentage of RhB is plotted against the time of contact whereby removal percentage is calculated by the formula [17]:

$$\% \text{removal} = \left(\frac{C_0 - C_e}{C_0} \right) * 100 \quad (11)$$

- Co: initial concentration (mg/L)
- Ce: equilibrium concentration (mg/L)

From the plotted graph the equilibrium concentration is deduced.

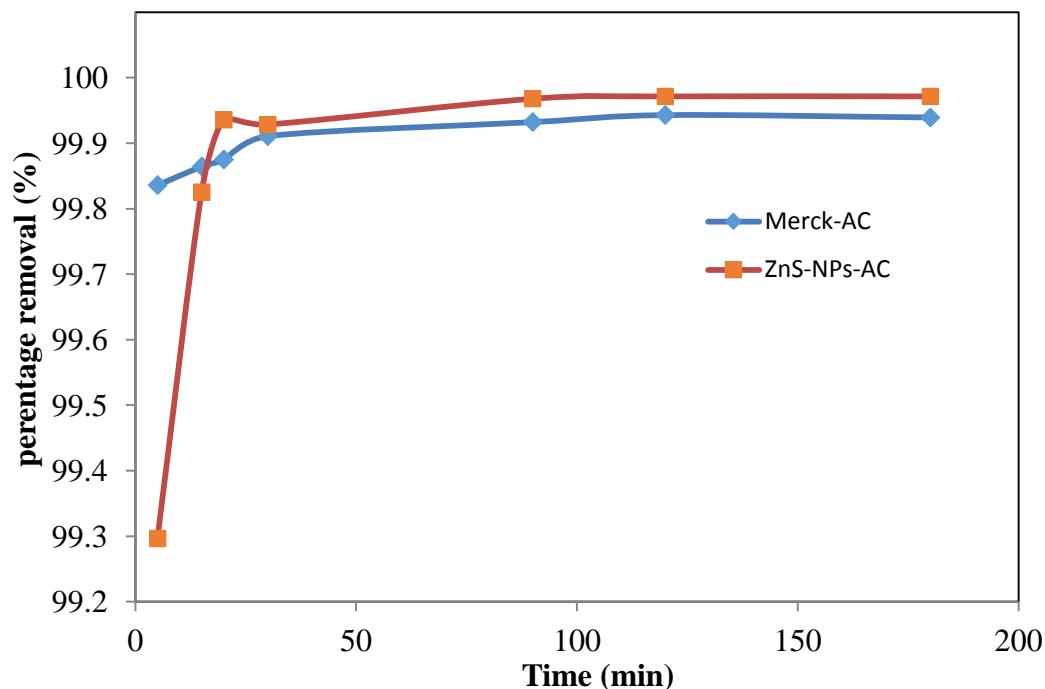


Figure 9. Effect of contact time Merck AC and ZnS-NPs-AC

From figure 9 the percentage removal of ZnS-NPs-AC shows a sharp increase from 5-20 mins from a value of 99.3 % to slightly above 99 %, which goes on to stabilise until 90 mins and remains constant from 90-180 mins, marking 90 mins to be the equilibrium time for ZnS-NPs-AC.

For the Merck-AC, the percentage removal slightly increases from a range of values of 99.8-99.9 % in the first 30 mins and stabilises up to 90 mins. From 90-180 mins the % removal is a fairly constant, with the difference between 90 mins and 120 mins being negligible, the equilibrium time also for the Merck AC is noted to be 90 mins.

III.3.2.2 Effect of dose

A good adsorbent has the ability to remove large amount of dye with a lower quantity of the adsorbent dose [17]. It is for this reason that the dose effect had to be studied for the two activated carbons, Merck-AC and Zns- NPs -AC.

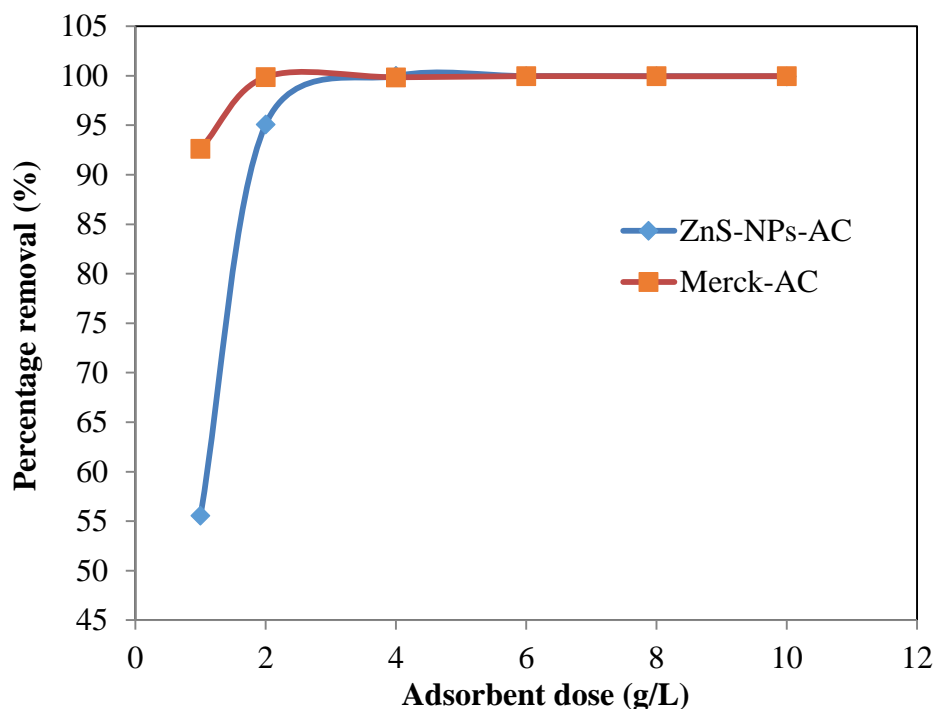


Figure 10. Effect of dose on yield removal of Rhodamine-B

Figure 10 goes on to show the result obtained for the dose effect for the two carbons. For the ZnS-NPs-AC, the adsorbent dose showed a sharp increase from 1 g/L to 2.5 g/L, with dye removal percentage increasing from 55-99 %. The adsorbent dose continued to stabilise up to 4 g/L and going on to show a fairly linear correlation from 4 g/L to 10 g/L. For the Merck-AC the adsorbent dose showed an exponential increase from 1 g/L to 2.5 g/L with the dye removal increasing from 93-99.9 % and showed a perfect linear correlation from 4 g/L to 10 g/L.

For both ZnS-NPs-AC and Merck-AC the optimal adsorbent dose was 4 g/L.

III.3.2.3 Effect of pH

In the adsorption processes by dyes the pH of the solution also has an impact of the removal percentage of the dye. This is due to the impact it has to the adsorption sites of the adsorbent and ionization process of the dye molecules. The study of the pH was done so as to find the optimal pH at which the two activated carbon were most effective in the removal of RhB.

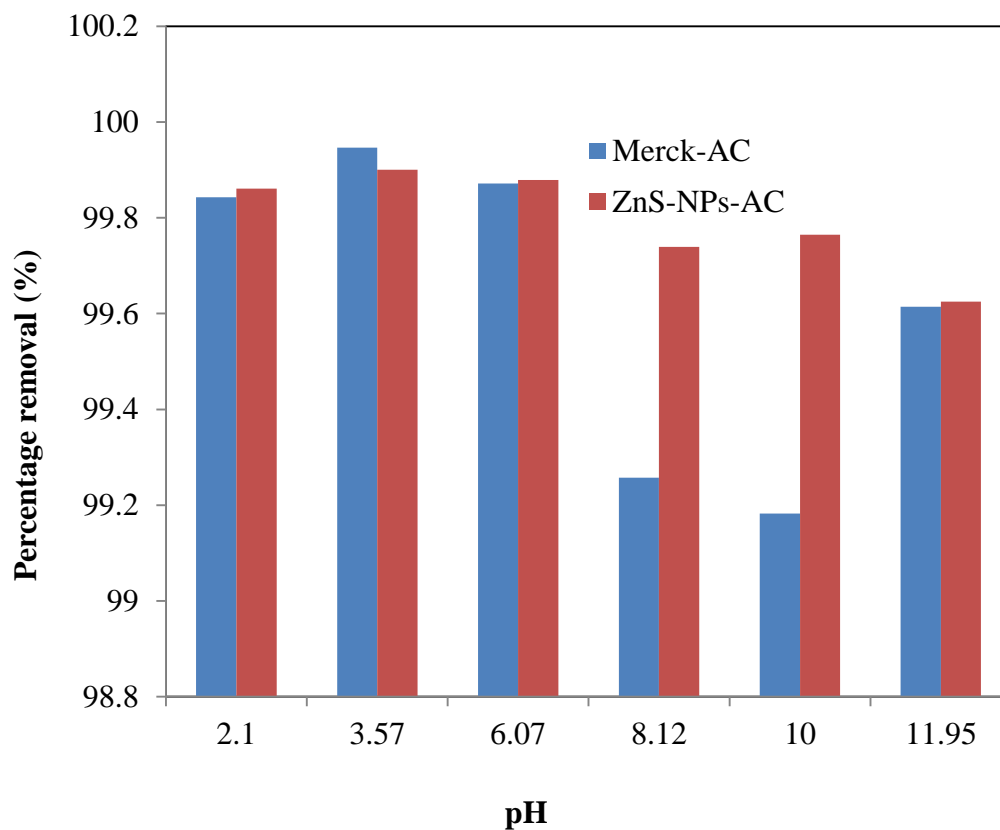


Figure 11. Effect of pH for removal of Rhodamine B with both Commercial AC and ZnS-NPs-AC

The pH effect was studied over a range of pH values between 2 and 12. Figure 11 shows the percentage removal for the two carbons varied in the range of slightly above 99.2 % to slightly above 99.8 %.

For both the Merck AC and ZnS-NPs-AC the optimal pH was 3.57 as this is the point where high percentage removal RhB of was achieved.

III.3.2.4 Kinetic adsorption experiments

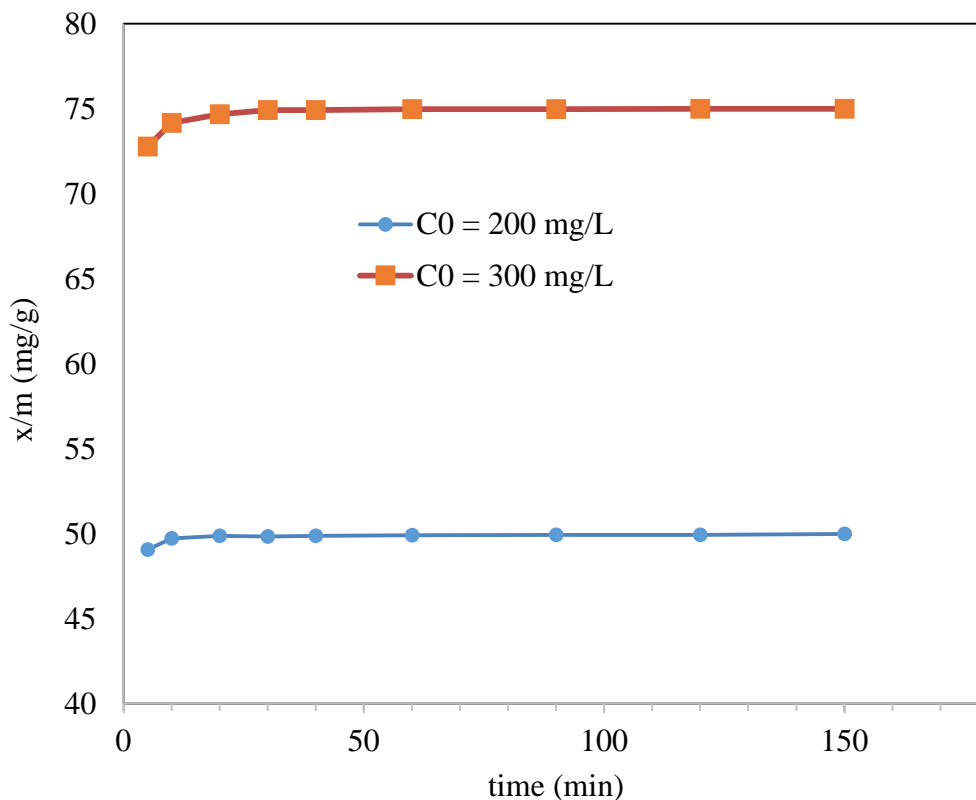


Figure 12. Adsorption kinetics for Commercial AC at two different concentrations

Figure 12 shows the adsorption kinetics for Merck AC at two concentrations, 200 mg/L and 300 mg/L where the amount of adsorbate adsorbed at equilibrium was noted to be 50 mg/g and 75 mg/g respectively.

Figure 13 below shows the adsorption kinetics for Merck AC at two concentrations, 200 mg/L and 300 mg/L where the amount of adsorbate adsorbed at equilibrium was noted to be 50 mg/g and 72 mg/g respectively.

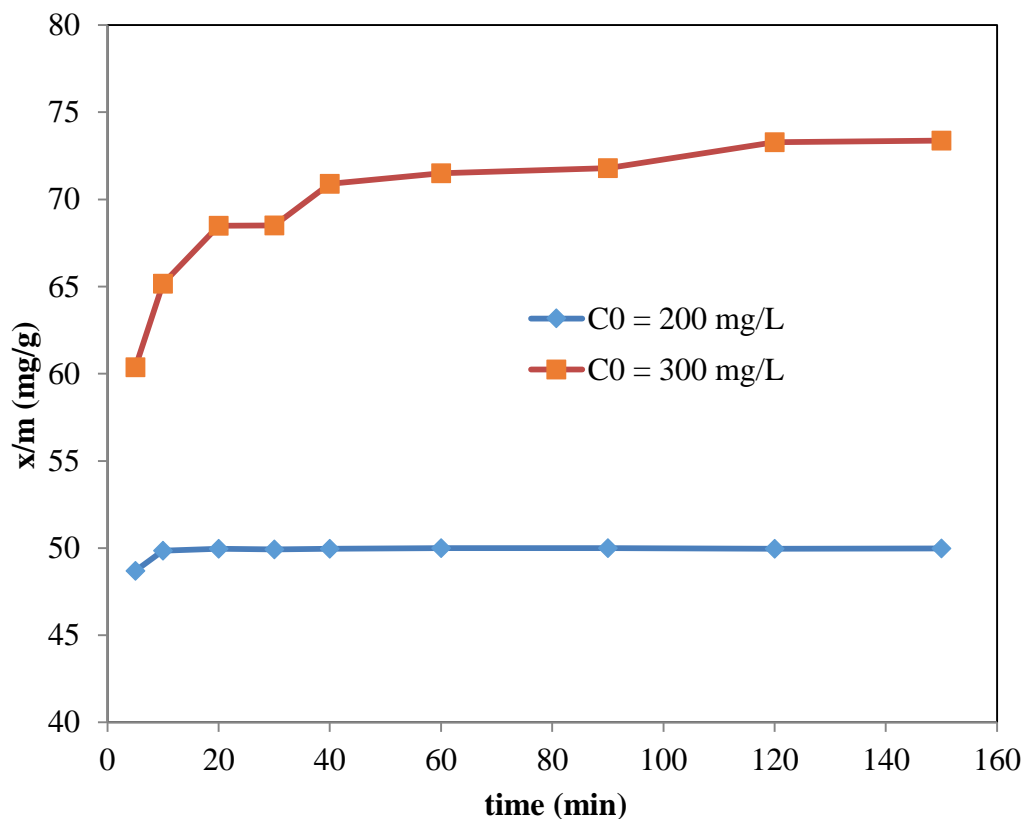


Figure 13. Kinetic adsorptions results for ZnS-NPs-AC for two different concentrations

III.3.2.5 Kinetic model results for Merck-AC

For a more detailed interpretation of the kinetic results, the kinetic models: the pseudo first order, pseudo second order and the intra particle diffusion are applied. The model having its conditions sufficiently met will be the appropriate kinetic model for the adsorption process

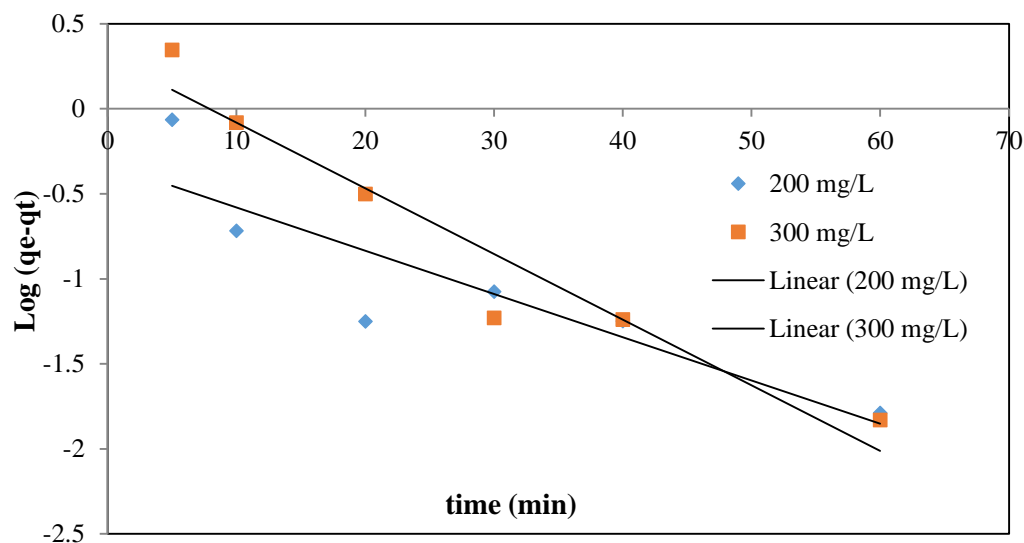


Figure 14. Pseudo first order Merck AC

For the pseudo first order model both concentrations show a linear correlation with a negative gradient upon tracing the line of best fit. For the 300 mg/L concentration, only two points are found to be directly on the line of best fit passing through $t = 10$ mins and $t = 40$ mins the rest of points are distant from the line of best fit with the point at $t = 30$ mins being extremely distant as compared to other points. The line of best fit for 200 mg/L passes only one point at $t = 30$ mins, with the rest of the plotted points being distant from the line of best fit with the points at $t = 20$ mins and $t = 5$ mins being outliers.

The results obtained graphically already suggest that the pseudo first order might not be the accurate model for this adsorption process.

Below are the results obtained for the pseudo premier order for the Merck AC:

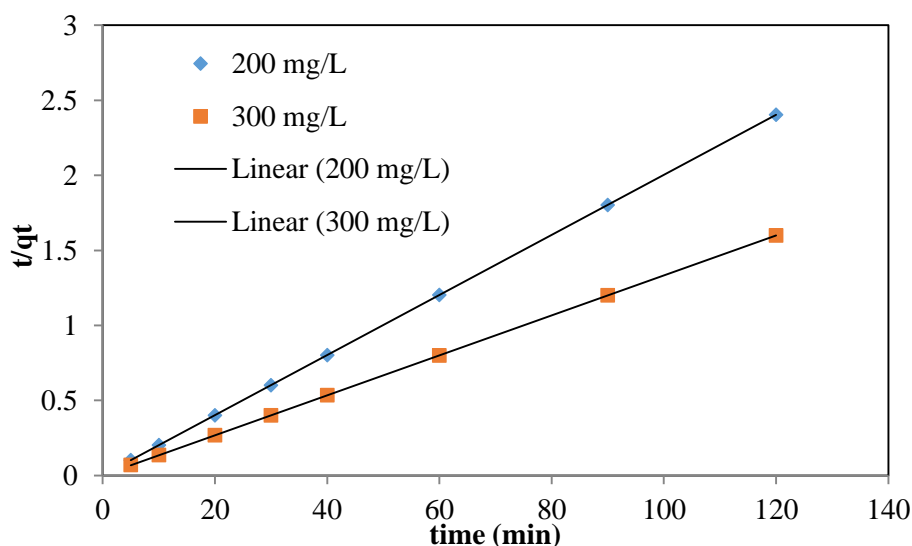


Figure 15. Pseudo second order for Merck AC

For the pseudo second order both concentrations for Merck AC showed a perfect liner correlation with a positive gradient. All plotted points resting perfectly on the line of best fit for both the concentration of 200 mg/L and 300 mg/L suggesting the pseudo second order to be the appropriate as compared to the pseudo first order.

For the study of the intra particle diffusion model Figure 16 below shows the results obtained for the Merck-AC at both concentrations of 200 mg/L and 300 mg/L.

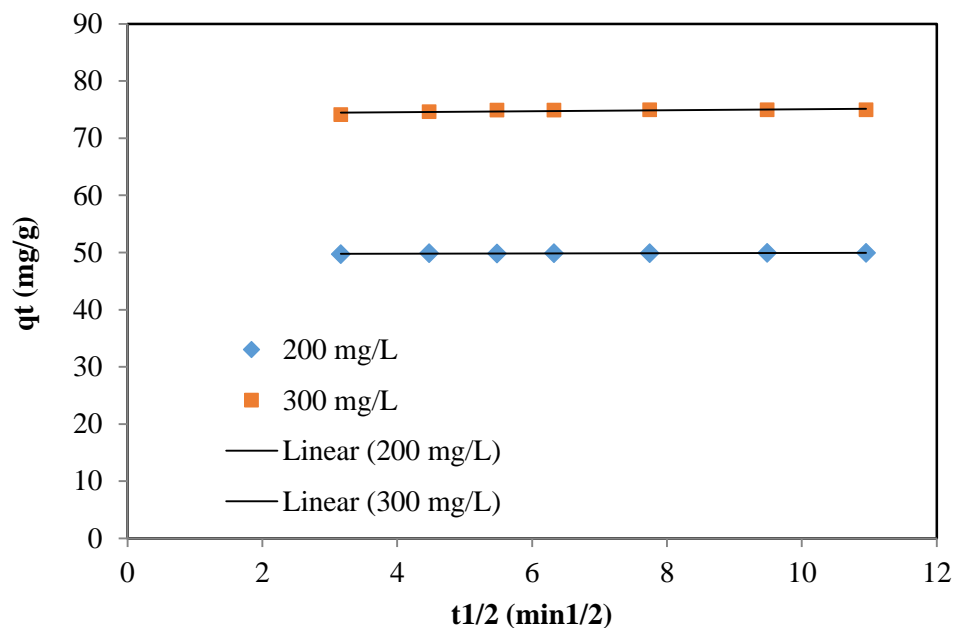


Figure 16. Intra particle diffusion model for Merck-AC

For the intra particle diffusion model both concentrations depicted a linear correlation with q_t remaining constant at 50 mg/g and 75 mg/g.

As both plots for the two concentrations did not pass through the origin the intra particle diffusion model is not the rate determining step and suggest also that boundary layer diffusion also took place in the adsorption process.

III.3.2.6 Kinetic model results for ZnS-NPs-AC

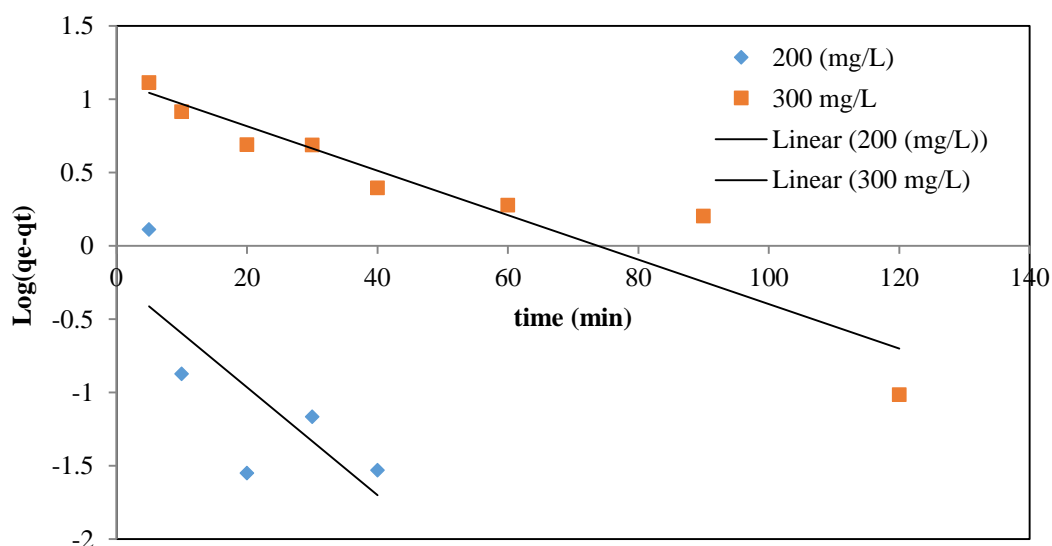


Figure 17. Pseudo-first order for ZnS-NPs-AC

For the pseudo first order the ZnS-NPs-AC both show a linear correlation with a negative gradient. The 300 mg/L plot showing to be more precise as compared to the 200 mg/L plot.

This conclusion is reached as by observation none of the plotted points fall on the line of best fit for the 200 mg/L plot and the deviation of these plotted points from the line of best fit is larger compared to the 300 mg/L plot.

Figure 18 below shows the kinetic results with the pseudo second order

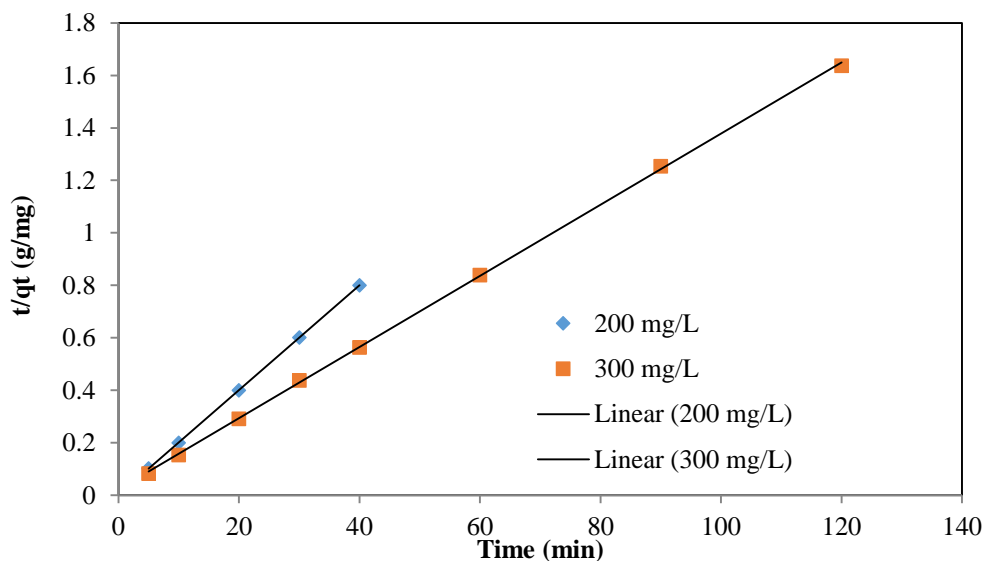


Figure 18. Pseudo-second order for ZnS- NPs-AC

For the pseudo premier order for the ZnS-NPs-AC, both concentrations show a perfect linear correlation with the line of best fit for each concentration passing through all the plotted points suggesting graphically that the suitable model is the pseudo second order.

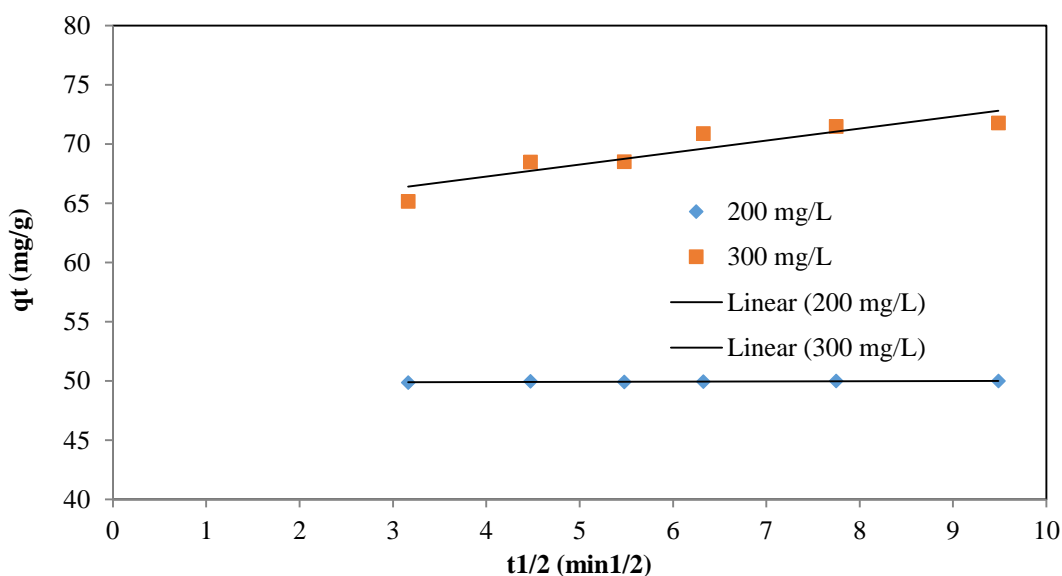


Figure 19. Intra particle model for ZnS-NPs-AC

For the intra particle diffusion model the two concentrations follow linear correlations with the 200 mg/L plot having a positive gradient and the 300 mg/L plot having a gradient of zero with q_t constant at 50 mg/g. As none of the two plots pass through the origin this implies also that the intra particle diffusion is not the rate determining step and also boundary layer diffusion also in the adsorption process.

Table 2. Parameters for determination of pseudo first order, second order and intra particle diffusion model for the two carbons.

Concentration (mg/L)	Pseudo-first order				Pseudo-Second order			Intraparticle diffusion		
	q_e (cal) mg/g	q_e (exp) mg/g	k_1 (min ⁻¹)	R^2	q_e mg/g	k_2 (gmg ⁻¹ min ⁻¹)	R^2	K_{dif} (mg min ⁻¹ g ⁻¹)	C (mg/g)	R^2
ZnS-NPs-AC 200	0.590	49.989	0.0847	0.596	50	0.222	1.00	0.0183	49.834	0.671
ZnS-NPs-AC 300	13.143	73.379	0.0350	0.885	73.529	0.0084	0.999	1.0163	63.180	0.840
Merck-AC 200	0.472	49.903	0.0254	0.790	50.00	0.307	1.00	0.0221	49.714	0.774
Merck-AC 300	2.021	47.963	0.0386	0.931	75.187	0.126	1.00	0.0842	74.225	0.580

Table 2 shows parameters of the kinetic models and the results obtained, the k_1 , k_2 , K_{dif} values obtained graphically, and the R^2 values which validate which model is the appropriate kinetic model to be used for this study.

For the ZnS-NPs-AC at concentration 200 mg/L the maximum adsorbate capacity q_e (exp) for the pseudo first order was lower than that of the pseudo second order model and the R^2 values was noted to be 1 for the pseudo second order which is a higher value than that of the pseudo first order noted to be 0.596. This proves the pseudo second order model to be appropriate for this adsorption process as the R^2 value for this model = 1, satisfying the condition for an excellent model which states that R^2 should be approximately or equal to 1, q_e (exp) also show the pseudo second order to be a more appropriate model than the pseudo first order model.

For the ZnS-NPs-AC at concentration 300 mg/L the pseudo second order is the more appropriate kinetic model as its R^2 value = 0.999 is closer to 1 and has a higher maximum adsorbate capacity as compared to the pseudo first order model.

For both the Merck-AC at 200 mg/L and 300 mg/L the pseudo second order is the appropriate model for this adsorption process as its R^2 values both = 1 and the maximum adsorbate capacity is higher for the pseudo second order kinetic model both concentrations as compared to the pseudo first order kinetic model.

For the intra particle diffusion the ZnS-NPs-AC, the R^2 values shows that the intra particle diffusion model mainly controlled the uptake of RhB at a concentration of 300 mg/L as compared to the concentration of 200 mg/L.

For the Merck-AC the R^2 values indicate that the intra particle diffusion controlled the uptake of RhB more at a concentration of 200 mg/L as compared to that of 300 mg/L.

III.3.2.7 Adsorption isotherm model graphs for Merck AC and ZnS-NPs-AC

For the determination of the isotherm type adsorption model graphs for both the Merck-AC and ZnS-NPs-AC were plotted. These adsorption isotherms found go on to describe the adsorption capacity and also the interaction between the adsorbent and adsorbate [18]. It's from the analysis of the shape of the graphical results of each model that the adsorption isotherm type it follows can be deduced.

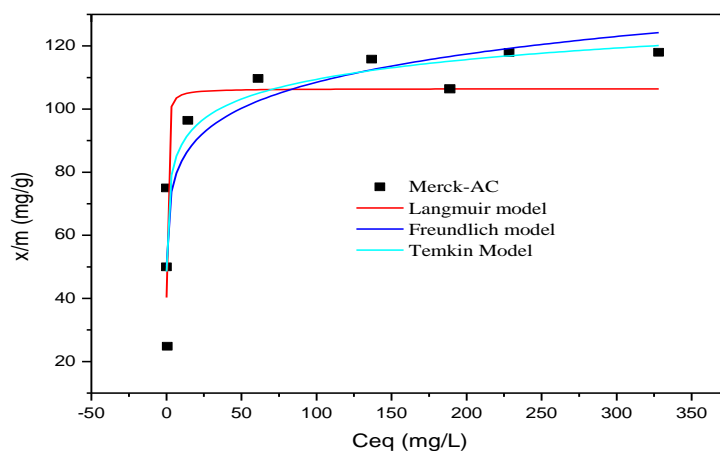


Figure 20. Graph for adsorption models for Merck-AC

For the Merck-AC the Langmuir model is initially vertical and after reaching a peak of 106 mg/g follows a linear correlation horizontally. This form goes on to show that the Langmuir model follows a type H isotherm which is seen when the adsorbed molecule and the adsorbent have strong interactions between them.

The Freundlich and Temkin model both show a downward concave shape at low concentration. This is an indicator of a reduction of free adsorption sites as the adsorption

process continues. This is a characteristic of a type L isotherm which takes place when the adsorbate molecule and adsorbent interactions are weak.

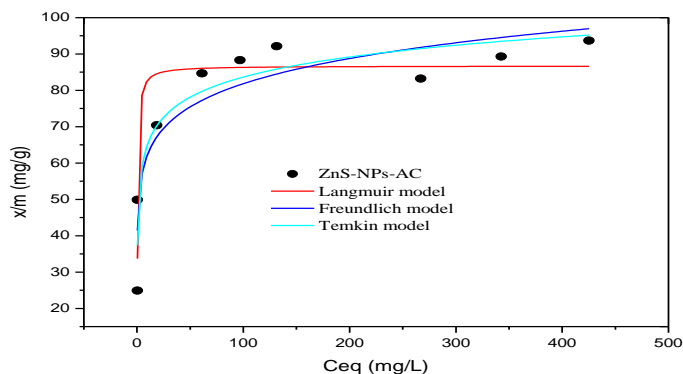


Figure 21. Graph for adsorption model for ZnS-NPs-AC

For the ZnS-NPs-AC the Langmuir model also follows the same shape for the Langmuir model for Merck-AC showing also that it is a type H isotherm the only difference being the Langmuir model for ZnS-NPs-AC reached a peak of 86 mg/g as compared to the Merck-AC which was 106mg/g.

The Temkin and Freundlich model for the ZnS-NPs-AC both show the same form as that of the Merck-AC. This shows that the Temkin and Freundlich models for ZnS-NPs-AC are of type L isotherm also.

Table 3. Adsorption parameters for the models for the two different carbons

Adsorbent	Freundlich			Langmuir			Temkin		
	Equation $q_e = K_F * C_e^{1/n}$			Equation $q_e = Q_{max}^0 * K_L * C_e / (1 + K_L * C_e)$			Equation $q_e = e * \ln(k_t * C_e)$		
	K_F (mg/g)	n	R^2	Q_{max}^0 (mg/g)	K_L (L/mg)	R^2	R^2	e	k_t (L/g)
Merck – AC	64.10964	8.75265	0.71671	106.47403	5.16621	0.33227	0.69345	9.02939	1832.31796
ZnS-NPs-AC	47.70451	8.53287	0.84162	86.71882	2.12275	0.87363	0.88624	7.97195	361.2562

For the Freundlich isotherm model, with the condition that $1 < n \leq 10$ [19], the results show a more favourable adsorption process for the Merck-AC as signified by the value of n which is greater than that of the ZnS-NPs-AC and a R^2 value of ZnS-NPs-AC greater than that of the Merck-AC.

For the Langmuir isotherm model, maximum adsorption capacity of the Merck-AC was found to be higher than that of the ZnS-NPs-AC. A given range of R_L values with a range of $0 < R_L < 1$ [20] are used to further describe results obtained for the Langmuir model.

For the Temkin isotherm model the values of e indicate the heat of sorption which indicates also the occurrence of a physical adsorption process, where $e = R_T/b_T$.

From the results obtained for Merck-AC the R^2 values obtained show that the adsorption process was better described by the Freundlich adsorption model which further means the adsorption was characterised by being multilayer on a heterogeneous surface. The R^2 values for the ZnS-NPs-AC show that the adsorption process is better described by the Langmuir adsorption model, as its R^2 value is closer to 1. This signifies adsorption being on mono layer on a homogenous surface.

Conclusion

From the results obtained the ZnS-NPs-AC has proved to have adequate porosity and can be used as effective adsorbent. The ZnS-NPs-AC had a high removal percentage of RhB of 99 % for an adsorbent dose of 4 g/L a maximum adsorbate capacity of 86 mg/g. The information obtained experimentally for the Rh-B dye adsorption fitted the Langmuir isotherm model and pseudo second order for the kinetic experiments. The adsorption process also follows the intraparticle diffusion model which was not the rate determining step. Boundary layer diffusion was also followed but from the R^2 values of the intraparticle diffusion model it is noted that the RhB dye uptake was majorly followed the intraparticle diffusion. In comparison with the documented performance of other adsorbents, the ZnS-NPs-AC nanocomposite used in this study showed good results at high physico-chemical characteristics.

From the results obtained the conditions of optimisation, the effect of pH can be labelled as not significant as the % removal was varying from 99.2 % to slightly above 99 % and also a shorter contact time can be used as the difference in % removal is negligible.

The reduction in maximum adsorbate capacity for the ZnS-NPs-AC as compared to the Merck-AC can be attributed to a decrease in porosity that might have been caused by the loading of the ZnS nanoparticle on the activated carbon.

Modifications for better efficacy can be further studied and made so as to improve the adsorption capabilities of the ZnS-NPs-AC by studying further the parameters affecting the adsorption process and the conditions at which the experiments were conducted.

The use of a photo catalyst and synergy can be used to improve the results obtained and better describe the adsorption process which was conducted.

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