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Study of Adsorption Efficiency to Remove Some of Azo Dyes Using Activated Carbon Derived From Agr-Residues.

This Thesis is submitted in Partial Fulfillment of the Requirements for the Degree of Master of Science in Chemistry, specialty of physical chemistry.

Submitted by:

Ayob Muftah Alfalos

Supervised by:

Dr. Khaled Ahmed Alfalos

Co-Supervised by:

Dr. Muktar Almabruk Aborziza

Dr. Fathy Mohamed Ahmed

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Dedication

Every challenging work needs self-efforts as well as guidance of elders especially dose who were very close to our heart.

My humble effort I dedicate to my sweet and loving

Father & Mother,

Whose affection love, encouragement and prays of day and night make me able to get such success and honor,

Along with all hard working and respected

Teachers

To everyone who cares about the environment and works to save it……

To everyone who inspires me by his/her science………

To my dear family

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In the name of Allah, the Most Gracious and the Most Merciful

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Ayob

الإقرار

أنا الموقع أدناه مقدم الرسالة التي تحمل العنوان :

Study of Adsorption Efficiency to Remove Some of Azo Dyes Using Activated Carbon Derived From Agr-Residues.

دراسة كفاءة الإمتزاز في إزالة بعض أصباغ الأزو بإستخدام الفحم المنشط الناتج من المخلفات الزراعية.

أقر بأن ما اشتملت عليه الرسالة انما هو نتاج جهدي الخاص، باستثناء ما تمت الإشارة إليه حيثما ورد، وأن هذه الرسالة ككل، أو أي جزء منها لم يقدم من قبل لنيل أية درجة علمية أو بحث لدى أية مؤسسة تعليمية أو بحثية أخرى.

Declaration

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

Student's name: إسم الطالب:

Signature: التوقيع:

Date: التاريخ:

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List of Abbreviation

Symbol	Abbreviation
A	Intra-particle diffusion constant gives an idea about the thickness of the boundary layer.
Abs	Absorbance.
AC	Activated carbon.
b	Langmuir constant related to the rate of adsorption.
C	Concentration of acetic acid at equilibrium.
C_0	Initial liquid-phase concentration of adsorbate.
C_{Ae}	The amount adsorbed on solid at equilibrium.
C_e	Equilibrium liquid-phase concentration of the adsorbate.
k_1	Equilibrium rate constant of pseudo-first-order kinetic model.
k_2	Equilibrium rate constant of pseudo-second-order kinetic model.
K_a	Ionization constant of weak acid.

K_d	The distribution coefficient.
k_c	Equilibrium constant
K_F	Freundlich constant represents the quantity of adsorbate onto activated carbon per a unit equilibrium concentration
k_p	Equilibrium rate constant of intra-particle diffusion kinetic model.
N	Number of moles of acetic acid adsorbed per 1.00g AC.
n	Freundlich constant gives an indication of how favorable the adsorption process is.
N_m	Number of moles of acetic acid per gram required to form monolayer
Q_o	Langmuir constant related to the adsorption capacity.
q_e	Amount of adsorbate per unit mass of adsorbent at equilibrium.
q_t	Amount of adsorbate per unit mass of adsorbent at time t (min).
R_L	Dimensionless equilibrium parameter
R	The universal gas constant (8.314 J/mol K).
R^2	Correlation coefficient.
SEM	Scanning Electron Microscopy.
XRD	X-ray diffraction
TGA	Thermogravimetric analysis
FT-IR	Fourier Transform Infrared Spectroscopy.
MS/Cs/An	modified seaweed (Posidonia oceanica)/Chitosan/Anthracene
$\Delta H°$	Standard enthalpy.
$\Delta S°$	Standard entropy.
$\Delta G°$	Standard free energy.

Abstract

Many different parts of the world have been facing the problem of dyes contamination of surface and ground water. Dyeing and printing industries are the main source of water pollution, Excessive use of dyes is considered to be the main reason for this contamination.

Therefore a simple, practical and economic process to reduce methyl orange dye concentrations in aqueous solutions with high adsorption capacity was the major objective of this research. To achieve this goal, adsorption experiments were conducted using activated carbon as adsorbent. The research method was used to minimize the cost of activated carbon production by preparation of (Modified Seaweed/ Chitosan solution/ Anthracene) composite. Modified Seaweed *(*MS*)* as starting material, was homogeneously mixed with Anthracene (An) (solid/solid ratio of 4/1) and then dissolved in Chitosan (Cs) solution, This minute quantity of (An) was selected to achieve the planned goal with minimal costs. The calcinated mixture was gently grounded for further application under the name of MS/Cs/An composite. The physicochemical properties of Modified Seaweed *(*MS*)* and (MS/Cs/An) composite were characterized via Fourier transform infrared spectroscopy FT-IR, X-ray diffraction XRD, and thermogravimetric analysis (TGA, DSC), Surface morphology and surface area were also examined using Scanning Electron Microscopy (SEM), and (BET) respectively**.**

The adsorptive properties of MS/Cs/An composite were investigated in terms of adsorbent dose, pH, temperature, contact time, and agitation speed. Experimental tests were conducted in a batch process.

The equilibrium adsorption data were interpreted using Langmuir, Freundlich, and Temkin isotherm models. The adsorption was found to follow Langmuir isotherm model. The calculated dimensionless separation factor, R_L

indicated that the adsorption of methyl orange onto adsorbent was favourable by the composite and the maximum monolayer adsorption capacity (q_{max}) was (37.04) mg/g. The MO distribution coefficient K_d decreased from 70.7 to 1.3 L g^{-1} with increasing initial MO concentrations from 20 to 80 mg L^{-1}. In order to investigate the adsorption mechanisms, three simplified kinetic models, i.e., pseudo-first-order, pseudo-second-order and intra-particle diffusion were applied to fit the kinetic data obtained by using experimental data of different initial concentrations. The rate constants for the three models were determined and the correlation coefficients were calculated. The kinetic data supports pseudo-second order model with an R^2 of 0.9999. The external (film) diffusion followed by intra-particle diffusion was the major driving process during the early stage of MO sorption. Various Thermodynamic parameters such as standard free energy (ΔG^0), standard enthalpy (ΔH^0), and standard entropy change (ΔS^0) of the adsorption process were calculated, which indicated that the present system was spontaneous, endothermic process in natural, and the adsorption is physicosorption.

The electrostatic interaction between the oxygen- and nitrogen-bearing functional groups on the MS/Cs/An surface and MO ions was the key controlling mechanism for the MO sorption process, particularly at $pH < pH_{PZC}$ of the composite. Meanwhile, valuable contributions from Yoshida and dipole–dipole H bonding mechanismscan explain the MO sorption by the addressed composite, especially at $pH > pH_{PZC}$.

Therefore, the developed composite is regarded as a better adsorbent to address industrial wastewater in Libya with low-cost and excellent efficiency.

Chapter One

Introduction

1.1 Environmental pollution

The most concerned environmental pollution is air pollution and wastewater pollution. Air pollution usually comes from open burning especially the forest and vehicles combustion while wastewater pollution comes from the industrial effluent and from the domestic sewage.

Wastewater pollution gives bad effects on public water supplies, which can cause health problem such as diarrhea, while air pollution can cause lung diseases, burning eyes, cough, and chest tightness.

Additionally, it is also an esthetic concern coursed by odors and discoloration, which interferes bathing facilities and recreation. It is also can cause property damage such as the discharge of sewage affects industrial water supplies by changing the character of the water. It is also affect real estate by causing paints to discolor as well as damage to boat, while ashes, smokes and dust can dirty and discolor structures and other property including clothes and furniture. Acid aerosols can eat away stone used on buildings, statues and monuments. Therefore, treatment of these pollutions is very important.

1.2 Wastewater pollution

One of the major environmental pollution is wastewater. Wastewater is the spent water after homes, commercial establishments, industries and public institutions, which used waters for various purposes. This polluted water comes from the domestic and from the industries since the increasing of population and industrial expansion especially from the developed countries.

These contaminants such as heavy metal, cyanide, toxic organics, nitrogen, phosphorous, phenols, suspended solids, color and turbidity from the industries and untreated sewage sludge from the domestics are become a great concern to the environment and public health. Table 1.1 shows the physical characteristics of wastewater and their sources (1).

Table 1.1 Physical characteristic of wastewater and their sources

Physical characteristic	Sources
Color	Domestics and industrial wastes, natural decay of organic materials
Odor	Decomposing wastewater, industrial wastes
Solids	Domestic water supply, domestic and industrial wastes, soil erosion, inflow-infiltration
Temperature	Domestic and industrial wastes

Decolorization of wastewater has become one of the major issues in wastewater pollution. This is because many industries used dyes to color their products, such as textiles, rubber, paper, plastics, leather, cosmetics, food and mineral processing industries at nearly 80% (2). Dyeing and printing industries are the main source of water pollution. It is reported that there are over 100,000 commercially available dyes with a production of over $7x10^5$ metric tons per year. Especially, the textile finishing industry has a specific water consumption (approx. 1L/kg of product), part of which is due to dying and rinsing processes. It has been estimated that about 9% (or 40,000 tons) of the total amount (450, 000 tons) of dyestuffs produced in the world are discharged in textiles wastewaters (3). Removing color from wastes is often more important because they have a synthetic origin and complex aromatic molecular structures, the presence of small amounts of dyes (below 1 ppm) is clearly visible and influences the water environment considerably (4).

In the present time, excessive released and production of wastewater as a product of various industries and other human activities is one of the major concern. This is due to the increasing demand of clean and potable water needed for various activities, human needs, and industrial production that in return produces a vast amount of wastewater.

Textile industry is a growing industry in the world, it accounts for the largest consumption of dyestuffs, and considered as one of the biggest consumers of water and complex chemicals during textile production. Different types of dyes are present in the effluents from textile industries, which has high molecular weight and complex structures that shows a low biodegradability (4). The textile industry discharge millions of liters of effluents directly into public drains which ultimately reaches fresh water. These effluents contains high amounts of grease, dirt, nutrients from dye bath, dye additives, residual dyes etc. 50% of textile effluent has residual azo dye (2).

The presence of dyes in wastewaters from industrial effluents and water supplies and their removal has received much attention in recent years due to the fact that many of them exhibit toxicity. Pollution by dyes is a serious threat to the aquatic ecosystem, which affects the quality of life and human health as well. Among the unwanted properties of dyes, resistance to natural degradation, allergenicity, carcinogenicity, and mutagenicity are all significant. They can also cause severe damage to human beings, such as dysfunction of kidneys, reproductive system, liver, brain and central nervous system hyperactivity in kids (ADHD), and deadly process of water eutrophication (5). The occupational exposure of workers in the textile industry is linked to a higher bladder cancer risk. Uses of hair coloring product and breast cancer have also been linked. Even in very small quantities, dyes can be very toxic and lead to changes in salinity and visible coloration of the water, reducing sunlight penetration and thus hindering the process of photosynthesis (6). Very strict laws regarding elimination of dyes from wastewaters before their discharge into water streams, together with the variety and minuscule concentrations of dye molecules make their satisfactory level of removing very difficult, requiring development of various technologies for dye elimination (7).

The discharge of dye effluents in water bodies poses direct and indirect consequences to aquatic ecosystem. The direct effects includes depletion of dissolved oxygen levels, decreased reoxygenation potential, leaching of dyestuff from soil into groundwater, reduced light penetration into water which hinders photosynthesis (which gives red signal to aquatic flora and fauna) and esthetic issue of water downstream (8).

Due to toxicity and mutagenicity of azo dyes, their removal from effluents has been an urgent challenge (9). Now days; research attention has been focused on biological methods for the treatment of effluents. The process continues until equilibrium is established between the amount of solid bound adsorbate species and its portion remaining in the solution. The degree of adsorbent affinity for the adsorbate determines its distribution between the solid and liquid phases. Various sorbents have already been used like mango peel, banana peel, coconut bunch waste, wheat husk, tree barks, tealeaf powder etc. (10). Much research work is being employed in determining new novel biosorbents for removal of azo dyes from effluent water

A dye may be defined as ―A colored substance which when applied to the fabrics imparts a permanent color and the color is not removed by washing with water, soap or an exposure to sunlight (11). Many dyes have been used in various dyeing process in textile industry and azo dye is one of them. The evolution of the chemistry of dyes began in 1856 with the discovery and industrial production of Mauve, by W.H. Parkin. Prehistoric man had already dyed furs, textiles and other objects with natural substances, mainly of vegetable, but also of animal origin. Further developments extending over many thousands of years led to rather complicated dyeing processes and high-quality dyeing. Most colored textiles and leather articles are treated with azo dyes and pigments (10). The commonly used azo dyes are Methyl orange and Methyl red.

Methyl orange (MO) is a kind of the p-aminoazobenzene (p-AAB) dyes. It is easily utilized in the textile stain industry and chemical experiments as well as an acid-base indicator in research laboratories and labs. However, the aqueous solution of MO is toxic and irritating. Thus, removal of MO from aqueous solution is of great weight and accomplished via different techniques (12, 13).

Improving an efficacious method for the administration and optimization of the dyestuff industry has long been the main target for environmental protection. In spite of the success of MO remediation at the laboratory scale based on photo-catalysis, electrochemical oxidation, and ultrafiltration techniques; at the industrial scale MO removal did not achieve the same success due to some economical and technical reasons. On the other hand, sorption techniques showed very good applicability in MO removal with high efficiency and reasonable costs (14).

The present work explored the utilization of MS/Cs/An composite for MO removal from aqueous medium under different physicochemical conditions to. (1) evaluate its MO removal efficiency, (2) assess the impact of the applied experimental parameters were conducted using a batch adsorption system; it was enhanced by applying the influence of important affecting factors such as (pH, amount of adsorbent, initial MO concentration, agitation speed, contact time, and temperature), (3) elucidate the mechanism and the behavior of MO sorption by fitting the experimental outputs to some well-known kinetic and isotherm models, and finally (4) assess the impact of the sorbed MO on the morphological characteristics of the sorbent MS/Cs/An composite.

The composite was been characterized by different analytical techniques such as (XRD), (SEM), (FTIR), (TGA, DSC) and BET analysis. In addition, the adsorption kinetics, isotherm, and thermodynamics were also investigated.

1.3 Technologies for color removal

There are different methods for the removal of pollutants (dyes, toxic elements etc.) from effluents (15).

Synthetic dyes in wastewater cannot be efficiently decolorized by traditional methods. This is because of the high cost and disposal problems for treating dye wastewater at large scale in the textile and paper industries (16).

In order to remove dye contaminants from water and to reduce the pollution effects of the dyes to environment, there are three kinds of treatment techniques for removing of the dyes from wastewaters. These are chemical, physical and biological treatment techniques (17). Chemical treatment techniques consist of two main divisions as advanced oxidation process (AOP) and chemical reduction. Advance oxidation includes some treatment processes like ozonation, fenton oxidation and photo catalytic oxidation. Chemical treatments contain also chemical reduction reactions. They convert hazardous polluting to nonhazardous or less toxic compounds. Second treatment technique is physical. It contains adsorption, ion exchange, irradiation, membrane filtration, electrolysis, coagulation/ flocculation and ultrasonic mineralization methods. The last treatment technique is biological, which includes bacterial and fungal biodegradation and biosorption in aerobic, anaerobic or combined treatment processes (18).

Table 1.2 shows a several reported methods for the removal of pollutants from effluents. All of them have advantages and drawbacks.

Table 1.2 Principal existing and emerging processes for dyes removal (19)

	Technology	**Advantages**	**Disadvantages**
Conventional treatment process	Coagulant-Flocculent	Simple, economically feasible	High sludge production, handling and disposal problems
	Biodegradation	Economically attractive, publicly acceptable treatment	Slow process, necessary to create an optimal favorable environment, maintenance and nutrition requirement

	Adsorption on activated carbon	The most effective adsorbent, great, capacity, produce a high-quality treated effluent	Ineffective against disperse and vat dye, the regeneration is expensive and result in loss of the adsorbent, non-destructive process
Establish recovery process	Membrane separation	Remove all dye types, produce a high-quality treated effluent	High pressure, expensive, incapable of treating large volumes
	Ion-exchange	No loss of sorbent on regeneration, effective	Economic constraints, not effective for disperse dye
	Oxidation	Rapid and efficient process	High energy cost, chemical required
Emerging removal processes	Advanced oxidation process	No sludge production, little or no consumption of chemicals, efficiency for recalcitrant dyes	Economically unfeasible, formation of by-products, technical constraints
	Selective bioadsorbents	Economically attractive, regeneration is not necessary, high selectivity	Requires chemical modification, non-destructive process
	Biomass	Low operating cost, good efficiency and selectivity, no toxic effect on microorganisms	Slow process, performance depends on some external factors (pH, salts)

Among the above-mentioned technologies, adsorption has been proven one of the most efficient and reliable methods for removing dyes from aqueous solution because of its flexibility, high efficiency, ease of operation, simplicity of design, and insensitivity to toxic pollutants (14). A wide variety of low cost and easily available materials, such as bentonite (20), fly ash (21), clay (22), active carbon (23), and agriculture wastes (24), have been exploited for the removal of dyes from aqueous solutions.

1.4 Problem Statement

Activated carbon has been the most popular and widely used adsorbent in wastewater treatment applications throughout the world. This is due to its high adsorption capacity, high surface area, microporous structure, and high degree of surface reactivity. In spite of its prolific use, activated carbon remains an expensive material since the higher the quality of activated carbon, the greater it costs. Therefore, this situation makes it no longer attractive to be widely used in small-scale industries because of cost inefficiency. Due to the problems mentioned previously, research interest into the production of alternative adsorbent to replace the costly activated carbon has intensified in recent years.

1.5 Strategic Objectives

In Libya, a dye contamination of wastewater comes from textile industries is becoming a major problem.

Therefore the overall goal of this research was to find practical and economical way to reduce dyes concentrations in wastewater that can be used in Libya and other Mediterranean countries.

1.6 Technical Objectives

This research was conducted to study the adsorption of azo dye, namely, Methyl Orange (M.O) using the cross-linked modified seaweed (Posidonia oceanica)/Chitosan/Anthracene composite in batch and continuous systems. The objectives of the research are to:

(i) Synthesize and characterize a low cost carbon adsorbent as alternative adsorbent materials from seagrass which can be used for water purification from dyes.

(ii) Study the adsorption azo dye (M.O) on cross-linked MS/Cs/An composite in batch process under varying operating conditions such as initial concentration, contaminant concentration, contact time, agitation speed, pH of solution and temperature.

(iii) Study removal efficiency of azo dye (M.O) on cross-linked MS/Cs/An composite from pre-contaminated aqueous solution.

(iv) Study the isotherm, kinetic and thermodynamic of azo dye adsorption on cross-linked MS/Cs/An composite.

1.7 Organization of the thesis

The thesis has been organized into several chapters:

Chapter 1 introduces world’s environmental issue and major environmental pollution is wastewater, technologies for color removal, problem statement, and objective of this work.

Chapter 2 reviews the fundamentals and previous findings. Subdivided into three sections, the first section introduces a general definition of dye and the treatment technologies for dye removal. Meanwhile, an overview of the adsorption process theory is presented in section two. Finally, section three gives review on the isotherm, kinetics and thermodynamic.

Chapter 3 presents the experimental procedures and analysis required in adsorption study. The first section describes the materials and chemicals used in the experiments. The second section presents description of equipment used for the batch experiment and the analysis system. The third section explains the experimental procedures and lastly the fourth section describes the analysis techniques performed for characterization of adsorbents.

Chapter 4 presents the experimental results together with the discussion. The detail explanations of the results have been divided into three main sections. The first section gives the results of adsorbent characterization. The second section presents the result and discussion for batch adsorption study including the effect of initial concentration, contact time, pH of solution and agitation speed. The second section discusses the thermodynamic studies. Finally, section three discusses the thermodynamic studies, adsorption isotherm and kinetic studies.

Finally, **Chapter 5** gives the conclusions and recommendations of the thesis.

Chapter Two

Literature Review

2.1 Color and the environment

Dyes and pigments are highly visible material. Thus, even minor release into the environment may cause the appearance of color, for example in open waters, which attracts the critical attention of public and local authorities. There is thus the requirement on industry to minimize environmental release of color, even in cases where a small but visible release might be considered as toxicologically rather innocuous. A major source of release of color into the environment is associated with the incomplete exhaustion of dyes onto textile fiber from an aqueous dyeing process and the need to reduce the amount of residual dye in textile effluent has thus become a major concern in recent years.

An alternative approach to addressing the problem of color in textile dyeing effluent has involved the development of effluent treatment methods to remove color. These methods inevitably add to the cost of the overall process and some present the complication associated with the possible toxicity of degradation products.

2.2 Colorants

Man has used natural colorants since prehistoric times. However, in 1856 Perkin's discovery of mauve which marked the start of the modern synthetic dye industry (25). Colorants are characterized by their ability to adsorb or emit light in the visible range (400-700 nm). Therefore, it is the reason they appear to be colored. In term of chemical structure, colorants can be divided into two groups, which are organic and inorganic colorants. Each of these groups can be further divided into natural and synthetic compounds.

Colorants include both dyes and pigments. Pigments are insoluble in the materials that they are used to color, whereas most dyes are soluble in them. The most important, difference between pigments and dyes is that pigments are used as colorants in the physical form in which they manufactured (26). Pigments particles have to be attached to substrates by additional compounds, such as by a polymer in paint. Dyes, on the other hand, are applied to various substrate (textile materials, leather, paper and hair) from liquid in which they completely, or at least partly, soluble. In contrast to pigments, dye must possess a specific affinity to the substrates for which they are used (26).

2.3 Dyes

Dyes are chemicals, which on binding with material will give color to the material. Dyes are ionic, aromatic organic compounds with structures including aryl rings which delocalized electron systems. The color of a dye is provided by the presence of chromophore group. They are widely used to color the substrate such as textile fiber, paper, leather, hair, fur, plastic material, wax, a cosmetic base or a foodstuff.

Dyes are large and important groups of chemicals. Today, there are more than 100,000 available commercially dyes, namely acid, reactive, disperse, vat, metal complex, mordant, direct, basic and sulphur dyes (27).

2.4 Toxicity of dyes

As the concentration of textile dye increases in water bodies, it stop the deoxygenating capacity of the receiving water and cut-off sunlight, thereby upsetting biological activity in aquatic life (28). Also, the photosynthesis process of aquatic plants or stage is affected. It has been observed that the chemicals used to produce dyes today are offered highly carcinogenic toxic and explosive effects on our environment. In addition to being toxic, dye effluents also contain chemicals that are carcinogenic, mutagenic or teratogenic to various organisms (29).This is especially serious because many chemicals can cause damage to genetic material without being expressed immediately .Dyes may affect the photosynthetic activity in aquatic life due to reduced light penetration and may also be toxic to some aquatic life due to the presence of aromatics, metals, etc. in them. It is reported that the mutagenic activity of textile wastewater effluents, using the salmonella/microsome assay and contributed the highest percentage (67%) of mutagenic effluents (30).

2.5 Classification systems for dyes

Dyes exhibit considerable structural diversity, and can be classified usefully in two separate ways, either accordance to their chemical structure or according to the method of application to the fiber type (dyeing method). Dyes must carry one or more functionalities giving the dye color, called chromophores, as well as an electron withdrawing or donating substituents that cause or intensify the color of the chromophores, called auxochrome. The chromophore group can be a base for dye classification. The most important chromophores are azo (–N=N–), carbonyl (–C=O), methine (–CH=), nitro (–NO_2) and quinoid groups. The most important auxochromes are amine (–NH_3), carboxyl (–COOH), sulfonate (–SO_3H) and hydroxyl (–OH) groups. In term of chemical structure, dyes may either be inorganic or organic compounds. Both groups can be further subdivided into natural and synthetic representatives.

2.5.1 Classification of dyes based on dyeing method

When classified according to dyeing method, one can be distinguish between anionic, direct, or disperse dyes, depending on whether these substances are used for dyeing protein, cellulose, or polysmide fibers. Furthermore, certain chemically reactive dyes can be used for different substrate, while for the same type of chemical structure are suitable for a single substrate only.

2.5.2 Classification of dyes based on their solubility

Dyes may also be classified according to their solubility: soluble dyes like acid, basic, metal complex, direct, mordant and reactive dyes or insoluble dyes including sulfur, azoic, vat and disperse dyes.

2.5.3 Classification of dyes based on their Chemical structure

According to the different groups dyes can be classified as follows (31).

a) Anthraquinoune dyes
b) Vat dyes
c) Indigoid
d) Polymethine dyes
e) Heterocyclic dyes
f) Aryl carboniumdyes
g) Phthalocyanin dyes
h) Sulphur dyes
i) Nitrosodyes
j) Diphenyla
k) Triphenylmethane dyes
l) Xanthenes dye
m) Azo Dyes
n) Nitro dyes

2.5.4 Classification of dyes based on commonly use

On the basis of their application mainly on fiber, commonly used dyes are given below (6):

a) Acid Dyes
b) Basic Dyes
c) Direct or Substantive Dyes
d) Mordant or Adjective Dyes
e) Vat Dyes
f) Sulphur Dyes

Table 2.1 summarized the application classes and their chemical types (25)

Table 2.1 The classification of dyes and chemical types

Class	Principle substrate	Method of application	Chemical types
Acid	Nylon, wool, silk, paper and leather	Usually from neutral to acidic dyebaths	Azo (including premetallized), anthraquinone,triphenylmethane, azine, xanthene, nitro and nitroso
Basic	Paper, polyyacrylonitrile, modified nylon, polyester and inks	Applied from acidic dyebaths	Cyanine, hemicyanine, diazahemicynanine, diphenylmethane, trialrylmethane, azo, azine, xanthene, acridine, oxazine, and anthraquinone

Direct	Cotton, rayon, paper, leather and nylon	Applied from neutral or slightly alkaline baths containing additional electrolyte	Azo, anthraquinone, styryl, nitro and benzodifuranone
Disperse	Polyester, polyamide, acetate, acrylic and plastics	Fine aqueous dispersions often applied by high temperature/pressure or lower temperature carried methods; dye may be padded on cloth and baked on thermofixed	Azo, anthraquinone, styryl, nitro and benzodifuranone
Reactive	Cotton, wool, silk, and nylon	Reactive site on dye reacts with functional group on fiber to bind dye covalently under influence of heat and pH (alkaline)	Azo, antraquinone, phthalocyanine, formazan, oxazine and basic
Solvent	Plastics, gasoline, varnishes, lacquers, stains, inks, fats, oils and waxes	Dissolution in the substrate	Azo, triphenylmethane, antraquinone, and phthacyanine
Sulfur	Cotton and rayon	Aromatic substrate vatted with sodium sulfide and reoxidized to insoluble sulfur containing products on fiber	Indeterminate structures
Vat	Cotton, rayon and wool	Water-insoluble dyes solubilized by reducing with sodium hydrogensulfite, then exhausted on fiber and reoxidized	Antraquinone (including polycyclic quinones) and indigiods

2.6 Azo dyes

The name azo comes from azote, the French name for nitrogen. They are compound bearing the functional group R-N=N-R' in which R and R' can be either alkyl or aryl groups. As a consequence of delocalization, aryl azo compounds have vivid colors specially red, orange and yellow so they are used as dyes and are commonly called as azo dyes.

Azo dyes are the largest group of dyes with large industrial application. Azo dyes stand for almost 70% of the textile dyestuffs produced by weight (32). They are used in the coloring process of several textiles, leather products, paper production, food industry, etc. and since they are known to transform to carcinogenic aromatic amines in the environment, their incorrect disposal is a major environmental concern and can affect human and animal health (33). As removal of azo dyes is of a particular interest for this review, general structure of azo dyes is represented in figure 2.1.

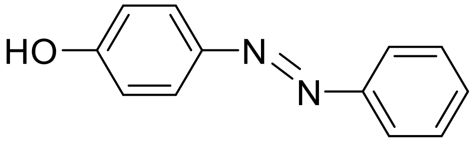


Fig 2.1: General structure of azo dyes

Azo dyes include at least one or more azo (N=N) double bond, with one or more aromatic systems Azo dyes are classified into two subgroups according to number of their double bond as mono-azo and poly azo types (34). Commonly used azo dyes are Methyl red and Methyl orange (35).

Methyl red Fig 2.2 is an azo dye prepared by diazotization of anthranilic acid followed by reaction with dimethylaniline

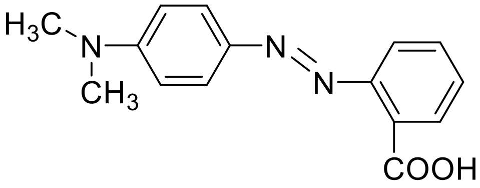


Fig 2.2: Methyl red

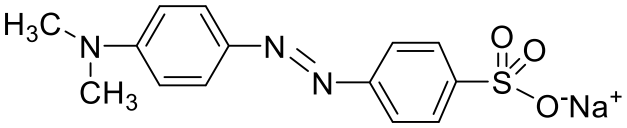


Fig 2.3: Methyl orange

Methyl red (2, (N-N dimethyl-4-aminophenyl) azo benzene carboxylic acid), also called as C.1. Acid red 2. It is dark red crystalline powder and red in pH under 4.4 and yellow in pH over 6.2. Its properties are summarized as in Table 2.2

Table 2.2 Properties of Methyl red

Properties	
Molecular formula	$C_{15}H_{15}N_3O_2$
Molar mass	269.30 g mol^{-1}
Density	0.791 g/cm^3
Melting point	179-182 °C,
pH	pH<4.4 pH>6.2
	red yellow

Methyl orange is sodium 4-[(4-dimethylamino) phenyl diazenyl] benzene sulfonate Fig 2.3. Reactive methyl orange is an anionic dye. It is also called C.1. Acid orange 52. It changes from red to orange yellow at pH 3.1 to 4.4. It is synthesized by reaction of sulfanilic acid, sodium nitrite. The diazonium salt so produced is coupled by dimethylaniline (7).Its properties are summarized as in Table 2.3.

Table 2.3 Properties of Methyl Orange

Properties	
Molecular formula	$C_{14}H_{14}N_3NaO_3S$
Molar mass	327.33 g mol^{-1}
Density	1.28 g/cm^3, solid
Melting point	>300 °C (Not precisely defined.)
pH	pH<3.1 pH>4.4
	red orange

2.7 Methods to remove dyes

Most dyes are non-biodegradable in nature, which are stable to light and oxidation. Therefore, the degradation of dyes in wastewater either traditional chemical or biological process has not been very effective (36).

Many conventional methods such as precipitation, ion exchange, solvent extraction, biosorption, filtration, electrochemical treatment have been applied for removal of contaminants from industrial wastewaters. These methods are either expensive or could not cope with high concentration of contaminants. All these methods have significant disadvantages such as incomplete ion removal, requirements and production of toxic sludge or other waste products that require further disposal. Therefore, these methods do not suit the needs of developing countries.

Adsorption process has been a prominent method of treating aqueous effluent in industrial processes for a variety of separation and purification purposes. This technique is also found to be highly efficient for the removal of color in terms of initial cost, simplicity of design, ease of operation and insensitivity to toxic substances (2). Therefore, adsorption using activated carbon is currently of great interest for removal of dyes and pigments.

The methods for dye removal can be divided into three categories: biological, chemical and physical Fig 2.4.

Generally in physical method dyes removed by adsorption, in chemical method chromophore has been modified through chemical reaction, biological method occurs through sorption and enzymatic degradation

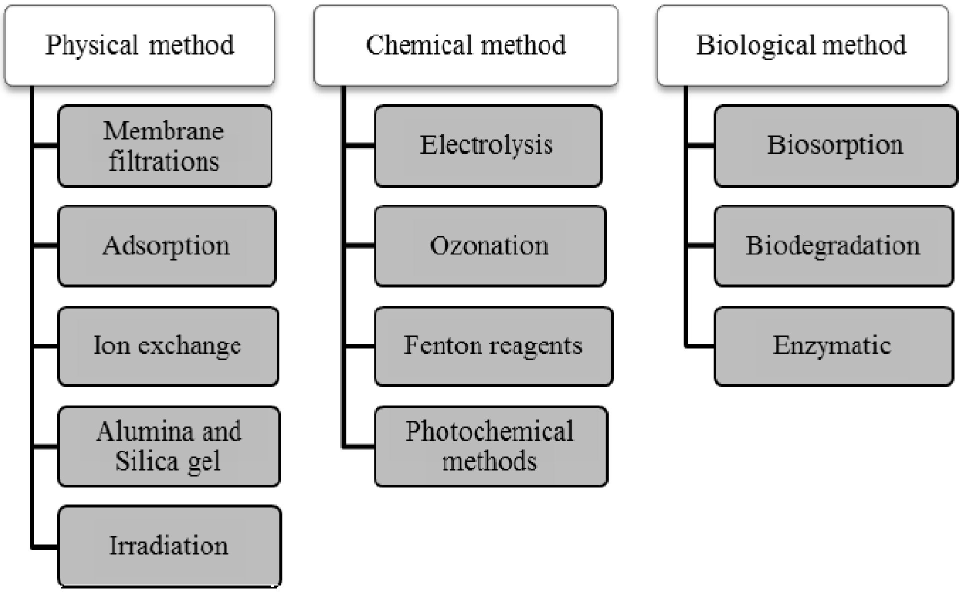


Figure 2.4: Techniques Involved in Removal of Textile Dyes

2.7.1 Physical methods

Different physical methods are also widely used, such as membrane–filtration processes (nanofiltration, reverse osmosis, electrodialysis) and adsorption techniques. The major disadvantages of the membrane processes are: (1) a limited lifetime before membrane fouling occurs and (2) cost of periodic replacement which need to be included in any analysis of their economic viability.

In accordance with the very abundant literature data, liquid-phase adsorption is one of the most popular methods for the removal of pollutants from wastewater since proper design of the adsorption process will produce a high-quality treated effluent.

This process provides an attractive alternative for the treatment of contaminated waters, especially if the sorbent is inexpensive and does not require an additional pre-treatment step before its application.

2.7.1.1 Adsorption technology

Adsorption is an essential process in the physiochemical treatment of wastewater, a treatment that can economically meet current effluent standards and water reuse requirements. Adsorption is a mass transfer process involving the accumulation of substances in a two phases interface, such as a liquid interface, liquid-gas, gas-solid, or solid-liquid. The substance being adsorbed is called adsorbate and the adsorbing material is described the adsorbent. The driving force of adsorption is surface affinity. pH, surface area and Chemical reactivity for adsorption per volume unit and reduction of surface tension are the main parameter of adsorption (37). Adsorption is a process in which the molecules of any state (gas or liquid) concentrate on the surface conduction without any interaction and it’s considered as the most effluent methods for removing of dyes from industrial wastewater by treatment due to ease of operation, low cost and efficiency (38). It has been pointed that the adsorption is an effective and attractive method because it can completely remove various types of dyes without leaving any fragments in the effluent (39).Adsorption depending on the nature of the adsorbate such as molecular structure, molecular weight, molecular size, polarity and solution concentration. In addition it also depends on the surface properties of the adsorbent material such as particle size, surface area, surface charge, etc. The process of adsorption is a highly efficient separation technique and is superior to other technologies available for wastewater treatment in terms of initial cost, simplicity of design, ease of operation and non-toxic materials. The efficiency of the adsorption process depends on the physical and chemical properties of the adsorbents and adsorbate. Adsorbent's selectivity depends on adsorption capacity, surface area, availability, and total cost (39). Commercial activated carbon is the most widely used as an adsorbent material in the dyes removal (39, 40).The selection of adsorbents depends on several factors (concentration and type of microstructure, efficiency/cost ratio, adsorption capacity, and high selectivity of a large amount of water). Moreover, these adsorbents should be non-toxic, low-cost, renewable, easily recoverable from alters, readily available, it should lead to zero waste sludge (41). An adsorbent material is a substance, usually porous in nature with a high surface area that can adsorb material on its surface by the intermolecular forces. Adsorbents are usually used in the form of spherical pellets, rods, moldings, or monoliths with hydrodynamic diameters between 0.5 and 10 mm.

They must have high resistance to abrasion, high thermal stability and small pore diameters, resulting in higher open surface area and therefore higher surface adsorption capacity. Adsorbents should also contain a distinct pore structure that allows the rapid transfer of gaseous vapors (42). The adsorbents are mainly derived from sources such as zeolite, coal, clay, ores and other waste resources. The adsorbents prepared from the waste resources used include petroleum wastes, coconut shell tannin-rich materials, sawdust, fertilizer waste, sugar industry wastes, blast furnace slag, chitosan and seafood residues, seaweed, algae, scrap tires, fruit wastes and peat moss as well as other adsorbents such as commercial activated carbon (CAC) (43). In addition to the mentioned above many natural materials were used as natural adsorbents such as orange peel as adsorbent for the removal of dyes from wastewater and to establish it as a standard wastewater treatment process for composite knit industry (44), rice husk (45), activated carbon (23), fly ash (21), papaya leaf (46), natural zeolite (47), chitosan films (48), calotropisgingantea (49), novel nonconventional activated carbon (50), peanut shell powder (51), cow dung ash (52), agricultural waste (24), sugar can stalks (53), modified pumice stone (54), quartenised sugar cane bagasse (55), nano aluminum oxyhydroxide (56) and ferric oxide (57).

2.7.1.2 Coagulation and Flocculation technology

Coagulation-flocculation is a frequently used physicochemical treatment method employed in textile wastewater treatment plants to decolorize textile effluent and reduce the total load of suspensions and organic pollutants (58).All waters, especially surface waters, contain both dissolved and suspended particles. Coagulation and flocculation processes are used to separate the suspended solids portion from the water. The suspended particles vary considerably in source, composition charge, particle size, shape, and density. Correct application of coagulation and flocculation processes and selection of the coagulants depend upon understanding the interaction between these factors. Coagulation and flocculation occur in successive steps intended to overcome the forces stabilizing the suspended particles, allowing particle collision and growth of floc (59).

Coagulation is a gelling or clumping of particle especially in a colloid (59). The first step in coagulation is to destabilizes the particle‘s charges. Coagulants with charges opposite those of the suspended solids are added to the water to neutralize the negative charges on dispersed non-settable solids such as clay and color-producing organic substances.

Once the charge is neutralized, the small suspended particles are capable of sticking together. The slightly larger particles formed through this process are called microflocs and they are not visible to the naked eye. Following the first step of coagulation, a second process called flocculation occurs. Flocculation, a gentle mixing stage, increases the particle size from submicroscopic microfloc to visible suspended particles. The microflocs are brought into contact with each other through the process of slow mixing. Collisions of the microfloc particles cause them to bond to produce larger, visible flocs called pinflocs. The floc size continues to build through additional collisions and interaction with inorganic polymers formed by the coagulant or with organic polymers added. Macroflocs are formed and once the floc has reached it optimum size and strength, the water is ready for the sedimentation process (59).

2.7.1.3 Membrane technology

The increasing trend of industrialization around the world has led to the generation of industrial effluents in large quantities, containing toxic organic substances, as well as large quantities of suspended materials (60). Membranes are widely used in different industries of separation processes because of their ability to control materials passing through the membrane, thus achieving a high degree of separation always, making these processes widely acceptable. The membrane is a barrier that allows certain substances to pass through it (permeate) while hindering others (retentate), in a rather specific manner (61). The significance of membrane technology in wastewater treatment is increasing. Membranes can be used to separate fluids, solids dissolved, suspended or dissolved in colloidal form. The main characteristics of the application of membrane processes in the treatment of consumables are the possibility of removing or recovering valuable or harmful components as well as the possibility of closing water systems, which reduces the consumption of fresh water. The use of membrane processes enables wastewater to be purified to a degree that is difficult to achieve through using of traditional techniques. The possibility of an application of pressure driven techniques such as ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) for oily wastewater treatment has been presented. Membrane technology offers a realistic solution to meet increasingly discharge limits and to reuse textile wastewater by providing treated water with good quality (62). Membrane technology has been used in treating secondary and tertiary municipal wastewater and oil field produced water. Membranes play an importance role in any advanced dye wastewater treatment system. Prevention of membrane fouling in these advanced membrane separation processes is considered as a critical challenge for ensuring their economic viability (63). Membrane technology display many applications at different stages of textile processing. These applications are unique because they provide a return on investment while abating the water pollution problem. The main stages of textile processing where membrane technology can be helpful are printing, scouring operations, dyes bath, latex recovery, sizing, and indigo recovery. Many researcher had been studied the role of membrane technology in wastewater treatment especially in textile industry. Nanofiltration is a membrane water treatment technique that finds its applications in wastewater and industrial water treatments such as in removal of colorants and organic matters and water softening (64). Cellulose acetate membrane in reverse osmosis process removed around 90% of color. GO-TiO_2 polymer membrane could make considerable improvement in the scope of water and wastewater treatment and could have important effects on the filtration efficiency (65).

2.7.1.4 Ion Exchange technology

Ion exchange is technique which involves an exchange of different ions between two electrolytes or between an electrolytic solution and an ion. Ion exchange is a process in which mobile ions from an external solution are exchanged for ions that are electrostatically bound to the functional groups contained within a solid matrix .There are different types of ion exchangers. Naturally Occurring Ion Exchangers (Natural inorganic ion exchangers, Natural organic ion exchangers), Synthetic Ion Exchangers (produced by creating chemical compounds with the desired physical and chemical properties and can be inorganic or organic based eg. Polystyrene divinylbenzene) and composite ion exchangers (consist of one or more ion exchangers combined with another material, which can be inorganic or organic and may itself be an ion exchanger) (66).

The management of waste from ion exchange membrane processes is mostly concerned with the further treatment of the concentrated salt stream, which can be treated by chemical methods or by evaporation or can be immobilized directly.

Ion exchange units are also sensitive to the presence of competing ions (66). Ion exchange is a very powerful technology to remove impurities from water and other solutions. Many industries depend on ion exchange for the production of extremely pure water.

2.7.2 Biological methods

Biological treatment is the most economical methods compared to other physical and chemical processes. Biodegradation methods such as fungal decolorization, microbial degradation, adsorption by (living or dead) microbial biomass and bioremediation systems are commonly applied to the treatment of industrial effluents because many microorganisms such as bacteria, yeasts, algaes and fungi are able to accumulate and degrade different pollutants (67). However, their application is often restricted because of technical constraint.

Microbial decoloration can occur via two principle mechanisms: biosorption and enzymatic degradation or a combination of both. Both reductases and oxidases are involved in the microbial degradation process. The goal of microbial treatment is to decolorize and detoxify the dye-contaminated effluents (68).

2.7.2.1 Biosorption technology

Biosorption is a metabolically passive process, means it does not require energy, and the amount of contaminants a sorbent can remove is dependent on kinetic equilibrium and the composition of the sorbents cellular surface. Biosorption is a property of certain types of inactive, dead, microbial biomass to bind and concentrate heavy metals from even very dilute aqueous solutions.

Biomass from algae, yeast, filamentous fungi and bacteria has been used to remove dyes by biosorption (69). The biosorption capacity of a microorganism is attributed to the heteropolysaccharide and lipid components of the cell wall, which contain different functional groups, including amino, carboxyl, hydroxyl, phosphate and other charged groups, causing strong attractive forces between the azo dye and the cell wall. The effectiveness of biosorption depends on the following conditions: pH, temperature, ionic strength, time of contact, adsorbent and dye concentration, dye structure and type of microorganism (70).

2.7.2.2 Enzymatic degradation

Azo dyes are electron-deficient xenobiotic components because of their azo linkage (-N=N-), and in many cases, they have sulphonic or other electron-z-withdrawing groups, which generate an electron deficiency and make the dye less susceptible to degradation by microorganisms. Under the appropriate conditions, they can be degraded by reductases. The anaerobic mechanism of microbial degradation of azo dyes to their corresponding amines is initiated by the cleavage of the azo linkage with the aid of an anaerobic azo reductase (71). Various enzymes that reduce azo linkages have been identified: FMN-independent reductases and NADPH-dependent reductases (72).

2.7.3 Chemical methods

Chemical methods including coagulation or flocculation combined with flotation and filtration, precipitation-flocculation with Fe(II)/$Ca(OH)_2$, electro-flotation, electro-kinetic coagulation, conventional oxidation methods by oxidizing agents (ozone), irradiation or electrochemical processes (73). These chemical techniques are often expensive, and although the dyes are removed, accumulation of concentrated sludge creates a disposal problem. There is also the possibility that a secondary pollution problem will arise because of excessive chemical use.

Recently, other emerging techniques, known as advanced oxidation processes, which are based on the generation of very powerful oxidizing agents such as hydroxyl radicals, have been applied with success for the pollutant degradation. Although these methods are efficient for the treatment of waters contaminated with pollutants, they are very costly and commercially unattractive. The high electrical energy demand and the consumption of chemical reagents are common problems.

2.7.3.1 Advanced oxidation processes (AOPs)

Synthetic dye wastes discharged from several industrial processes pose a major threat to the environment due to the risk of toxicity to aquatic organisms in natural water resources and inhibition of photosynthetic activity. Many researchers proposed advanced oxidation processes (Ozone, H_2O_2, TiO_2, ZnO, RuO_2, SiO_2 and UV) as a reasonable option for efficient removal of color pollutants from wastewater. Advanced oxidation processes including TiO_2/UV and H_2O/UV were demonstrate for their potential use in dye removal from textile wastewater (74). Advanced Oxidation Process (AOP) is a chemical treatment method that grows in the wastewater management industry. It is suggested way to remove organic matter. The basic principle of AOP includes the production of hydroxyl radicals ($OH^\bullet$), which can be generated from hydrogen peroxide (H_2O_2), ozone, photo-catalysis or oxidizing agents together with the use of ultraviolet rays. The $OH^\bullet$ is primarily responsible for the decomposition of organic compounds (75). Advanced oxidation processes (AOPs) have already been used to treat wastewater containing t organic matters such as, surfactants, insecticides ,coloring matters, pharmaceuticals and endocrine disrupting chemicals,. In addition, they have been successfully used as pre-treatment methods to reduce concentrations of toxic organic compounds that inhibit biological wastewater treatment (76). The most common advanced oxidation processes (AOPs) of treatment is using of UV wavelengths (200-300) nm at 254 nm to disassociate H_2O_2 progressively. The UV/H_2O_2 systems generate hydroxyl radicals ($OH^{\bullet}$), which are highly powerful oxidizing species. The main advantages of advanced oxidation processes involve the lack of by-products that may cause secondary pollution, elimination of the hazard of overdosing the oxidizing agents, and high process rate and efficiency (77).

2.7.3.2 Ozone (O_3)

Ozone is one of the most powerful and commercially available oxidizing substances and is commonly used for municipal water treatment and wastewater. In addition to the oxidizing capabilities of ozone, it is considered as an environmentally friendly method of treatment. Contaminants, colored substances, odors and microorganisms are destroyed directly by oxidation, without creating harmful chlorinated by-products or significant residues (78). Ozonation is particularly attractive for wastewater treatment because ozone, is soluble in water and can decompose quickly to form several free radicals including $OH^{\bullet}$ (hydroxyl), $HO_3^{\bullet}$, $HO_4^{\bullet}$ and O_2^- (superoxide). Such free radicals are readily available to react instantly with any organic compounds present in water, like the dyes. Therefore, the using combination of ozonation and biological degradation process may provide more economical and effective process in the treatment of highly colored wastewater (79).

2.7.3.3 Fenton Oxidation technology

Among several of AOPs, the Fenton reagent (H_2O_2/Fe^{+2}) is one of the most effective ways to oxidize of organic pollutants. The Fenton reagent has been found to be effective for treating of various industrial wastewater compounds, including aromatic amines, a wide range of dyes, and different other substances, e.g. pesticides and surfactants insecticides. Therefore, the Fenton reagent has been applied for treating a variety of waste such as those associated with textile and chemical industries (80). Fenton process is based on OH production as a result of interaction between Fe^{+2} and H_2O_2 under acidic conditions. The process was improved using different sources of iron such as iron powder. The reaction of Fenton, in which Fe^0 is used mainly, can be implemented in two ways, the one is oxidation of the pollutant as a result of H_2O_2 reaction on the iron surface, and the other one is oxidation of the contaminated H_2O_2 reaction with Fe^{+2}, which is transferred to the liquid phase by dissolving on the iron surface. The Fenton reagent was found to target water-soluble, nucleophilic and aromatic contaminates (81).

2.7.3.4 Ultraviolet Lamp

Ultraviolet light is a part of the spectrum light. The process usually includes using of low-pressure UV lamps with a principal wavelength of 254 nm. The maximum absorption of ozone molecules is at 253.7 nm, the light source commonly used is a medium-pressure mercury lamp wrapped in a quartz sleeve that can generate the UV light at wavelength of 200-280 nm .Application of UV lamp for textile wastewater treatment with two different UV radiations; 150W, λ= 254-578 nm and 15W, λ= 254 nm, to the synthetic textile wastewater for 1 to 3 showed significant reduction (47 to 30%) in microbial inhibitory action for optimum radiation time of 1 hour (82).

2.7.3.5 Peroxone (H_2O_2/O_3)

H_2O_2 acts as a catalyst and accelerates the decomposition of ozone to hydroxyl radical when a mixture of hydrogen peroxide and ozone is used to treat wastewater. At acidic pH, H_2O_2 reacts very slowly with O_3 whereas at high pH the dissociation of H_2O_2 into HO_2 (83).

2.7.3.6 Electrochemical technology

In recent years electrochemical technologies have been attracted much attention due to the distinctive features of environmental compatibility, safety and versatility. Electrochemical technology competes with other conventional technologies including precipitation, evaporation, ion exchange and solvent extraction to offer solutions to the needs of the different industries (84). Electrochemical technologies been used by researchers for the efficient treatment of wastewater in textile industry (85). Generally electrochemical technologies are cleaner than physicochemical and membrane technologies especially in color removal from wastewater because it's using the electron as unique reagent and do not produce solid residues (86). The process is based on the direct degradation of dye on the anode using chloride as electrolyte and on the indirect oxidation of dyes using the generated species. Electrochemistry offers promising methods to prevent pollution problems in the process industry. The feasibility of electrochemical conversion/destruction of organic substrates in wastewater has attracted much attention since pioneering studies to our times (87). The efficiency of electrochemical method based on the nature of the selected anode and stable anodes that are prepared by the precipitation of thin layer of metal oxides on a base metal. Numerous researchers have investigated electrochemical oxidation for degradation of azo dye through optimization of operating parameters using various anodes including RuO_2, SnO_2, PbO_2 and diamond electrode (88). various advantages of Electrochemical technologies involve high efficiency, easy in operation and handling, automation, simple equipment, safety, operations under ambient temperature and pressure conditions (89). Electrochemical technologies no need of chemical requirements, occupying a small area in plants and simple operation and not producing any sludge. In addition to the mentioned above its utilization of a green reagent such as the electron, extremely high removal of multiple contaminants, effective disinfection, high flexibility and no necessity to transport or stock chemical oxidants (90).

2.8 Theory of adsorption

2.8.1 A Brief History of Adsorption

The ability of some solids to remove color from solutions containing dyes has been known for over a century. Similarly, air contaminated with unpleasant odors could be rendered odorless by passage of the air though a vessel containing charcoal. Although such phenomena were not well understood prior to the early twentieth century, they represent the dawning of adsorption technology which has survived as a means of purifying and separating both gases and liquids to the present day. Indeed, the subject is continually advancing as new and improved applications occur in competition with other well-established process technologies, such as distillation and absorption.

Attempts at understanding how solutions containing dyes could be bleached, or how obnoxious smells could be removed from air streams, led to quantitative measurements of the concentration of adsorbable components in gases and liquids before and after treatment with the solid used for such purposes. The classical experiments of several scientists including Brunauer, Emmett and Teller, McBain and Bakr, Langmuir, and later by Barrer, all in the early part of the twentieth century, shed light on the manner in which solids removed contaminants from gases and liquids. As a result of these important original studies, quantitative theories emerged which have withstood the test of time. It became clear, for example, that the observed effects were best achieved with porous solids and that adsorption is the result of interactive forces of physical attraction between the surface of porous solids and component molecules being removed from the bulk phase. Thus, adsorption is the accumulation of concentration at a surface (as opposed to absorption which is the accumulation of concentration within the bulk of a solid or liquid).

Industrial applications of adsorbents became common practice following the widespread use of charcoal for decolorizing liquids and, in particular, its use in gas masks during the 1914–18 World War for the protection of military personnel from poisonous gases (91), Adsorbents for the drying of gases and vapors included alumina, bauxite and silica gel; bone char and other carbons were used for sugar refining and the refining of some oils, fats and waxes; activated charcoal was employed for the recovery of solvents, the elimination of odors and the purification of air and industrial gases; fuller's earth and magnesia were found to be active in adsorbing contaminants of petroleum fractions and oils, fats and waxes; base exchanging silicates were used for water treatment while some chars were capable of recovering precious metals. Finally, some activated carbons were used in medical applications to eliminate bacteria and other toxins (92). Equipment for such tasks included both batch and continuous flow configurations, the important consideration for the design of which was to ensure adequate contact between adsorbent and fluid containing the component to be removed (the adsorbate).

2.8.2 Definition

Adsorption is a surface phenomenon, which arises due to interactions between the individual atoms, ions or molecules of an adsorbate and those present in the adsorbent surface. Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (the adsorbate). The process involves an array of phenomena that can alter the distribution of the solute among the constituent phases and in the interfaces (93). The process is accompanied by separation of the solute from one phase to another following its accumulation at the surface of the latter Fig 2.5.

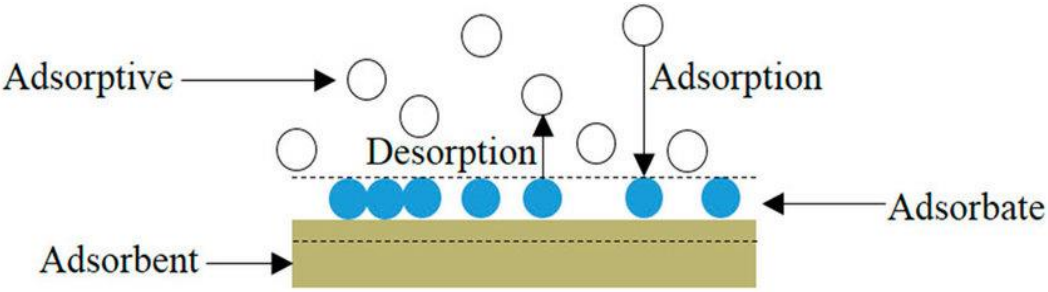


Fig 2.5 Adsorption process

2.8.3 Types of Adsorption

Depending upon the nature of force existing between adsorbate molecule and adsorbent, two types of adsorption can be distinguished:

a) Physical adsorption or Physisorption:

This type of adsorption results from the action of weak van der Waals forces. These are comprised of London dispersion forces and classical electrostatic forces that are related with interactions between the dipole moments of adsorbate and adsorbent molecules. This type of adsorption is non-specific, i.e. the adsorbent does not have preference for any particular gas (94).

b) Chemical adsorption or Chemisorption:

Chemical adsorption involves strong adsorbate-adsorbent interactions resulting in a change in the chemical form of the adsorbate. Here, the gas molecules or atoms are held to the solid surface by chemical bonds. The resulting chemisorptive bond is generally stronger than that derived from the physical van der Waals forces and is very similar in strength to a covalent bond. It is highly specific and occurs only if there is some possibility of chemical bonding between adsorbent and adsorbate. The bonds that form between solute molecules and specific surface chemical groups have all the properties of true chemical bonds and are characterized by relatively large heats of adsorption (95).

The differences between the two types of adsorption can be summed up using several criteria shown in the following table 2.4

Table 2.4 The differences between physical and chemical adsorption (95)

Properties	Physical adsorption	Chemical adsorption
Bonding	The forces operating in this case are weak Vander wall's forces.	The forces operating are chemical bonds (ionic, covalent or hydrogen bond).
Heat of adsorption	The heat of adsorption is low about 20-40 Kj $rnol^{-1}$.	The heat of absorption are high about 40-400 Kj $rnol^{-1}$.
Nature of the Process	The process is reversible, desorption can be occur by increasing ternp. or	The process is irreversible. Efforts to free the adsorbed gas

	decreasing pressure	give different compounds
Activation energy	It does not require any activation energy.	It requires activation energy.
Temperature condition	It takes place at the low temperature and decreases with increase in the temperature.	This type of adsorption first increases with increase in temperature.
Specificity	It is not specific in nature all gases adsorbs on all solids to same extent.	It is highly specific in nature occurs only by the possibility of formation of chemical bond.
Surface area	It increases with the increase in surface area of the adsorbent.	It also increases with the increases with the increase in surface area of adsorbent.
Molecular layers	It forms multi-molecular layer.	It forms unimolecular layer.

2.8.4 Mechanism of Adsorption

Adsorption acts as a separation process which means an involuntary process and an exothermic process that liberates energy. Thus, it is costly due to the need of chemicals, energy and the separation agent or sorbent. The surface of the adsorbent and the pore size of adsorbate molecule are playing the important role in determining the effectiveness of the adsorption process. Besides, a minimum amount of energy should be supplied to provide a good contact between the liquid and the surface of adsorbent under certain conditions to obtain the equilibrium state, thus encouraging or limiting the diffusion limitations (96).

The adsorption process consists of four steps as shown in Fig 2.6; the first step will be the bulk solution transport. This step involves the movement of the substance to be adsorbed through the bulk liquid to an extremely thin surface layer of the adsorbent. This is followed by the second step, film diffusion transport, where by the substance is diffused to the entrance of the pore of adsorbent through the stagnant liquid film. In the third step, pore transport will occur. In this step, the substance will be adsorbed through the pores and along the surface of the adsorbent. Lastly, the forth step will be the adsorption in which the adsorbate adheres to the surface of the adsorbent at an available adsorption site (97).

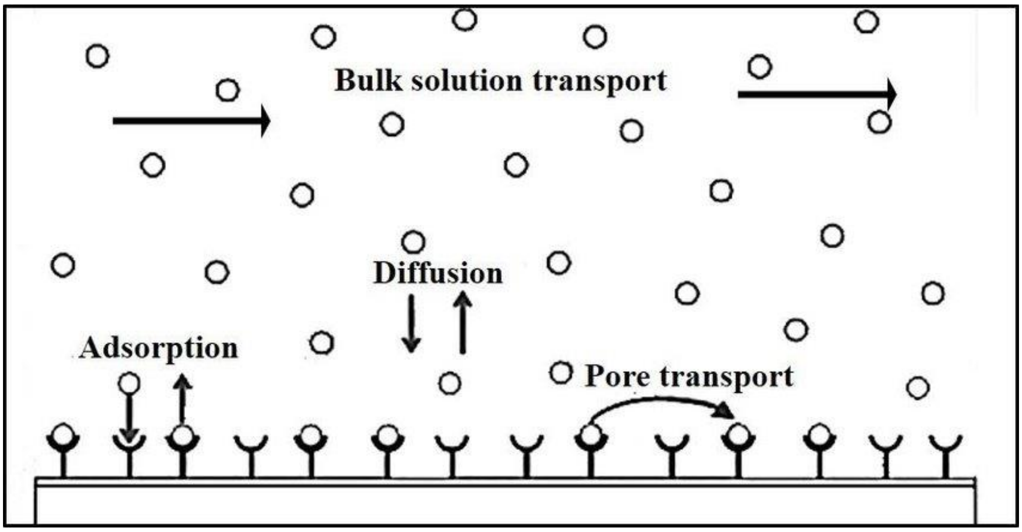


Fig 2.6 Schematic diagram of adsorption mechanism

2.8.5 Factors influences the extent of adsorption

The process of adsorption is affected by several factors such as the internal surface area of adsorbent, pH, the mass of adsorbent, the initial concentration of adsorbate and temperature. Some of these are:

a) Characteristics of the adsorbent

The adsorbent must have good mechanical properties such as strength and resistance to attrition and it must have good kinetic properties, that is, it must be capable of transferring adsorbing molecules rapidly to the adsorption sites. An adsorbent material must have a high internal volume, which is accessible to the components being removed from the solvent. Surface area and the distribution of area with respect to pore size are two very important factors in determining extent of adsorption. The nature of the intra-particle surface area markedly influences the types of adsorption process (98).

b) Characteristics of the adsorbate

The extent of adsorption relates to certain properties of the adsorbate relative to the solution phase, namely surface tension and solubility. The extent of adsorption is influenced by the solvophobicity or lyophobicity of a component in the solvent phase (98).

c) Characteristics of the solution

In the presence of aqueous phase, hydrogen ions and hydroxide ions often interact with adsorbents used in the system. Thus the adsorption process may be affected by solution pH. The pH causes the ionization of active sites, hence affecting the removal performance. As the value of pH is below 3, there will be a little sorption due to the carboxylic sites are mainly protonated, thus causing less sites for the adsorption process. As pH increases, the efficiency of adsorption increases due to the deprotonation, thus increasing the negative charge density on the sorbent surface (99).

The temperature can also remarkably influence adsorption process. The rate of adsorption usually increases with temperature (for an endothermic process) which is due primarily to the increased rate of diffusion of adsorbate molecules through the solution to the adsorbent. Temperature effects solubility which in turn affects the extent of adsorption. The presence of competing adsorbate molecules often influences the extent of adsorption. Few adsorbents demonstrate controllable selectivity for specific adsorbates and thus, all adsorbable compounds present will compete for adsorption sites (99).

2.8.6 Types of Adsorbents

Different types of conventional and non-conventional adsorbents have been used in the laboratory as well as for industrial purposes. Some of these are:

I. Conventional Adsorbents

- **a)** Activated carbon
- **b)** Carbon molecular sieves (CMS)
- **c)** Carbonized polymers and Resins
- **d)** Bone charcoal
- **e)** Polymeric Adsorbents
- **f)** Silica gel
- **g)** Activated alumina
- **h)** Clay minerals
- **i)** Zeolites

II. Non-conventional adsorbents

a) Adsorbent from industrial wastes
b) Adsorbent from coal
c) Adsorbent from agricultural wastes and agricultural byproducts
d) Peat
e) Oxides and related materials as adsorbents
f) River sediments as adsorbent
g) Adsorbent from bio-resources
h) Adsorbent made from biopolymers such as chitosan
i) Adsorbents form various other materials

2.8.7 Selectivity of an Adsorbent

To be technically effective in a bulk separation or a purification, an adsorbent material must possess some unique characters such as high internal volume, high surface area, porosity, appropriate pore structure and suitable adsorbing surfaces, etc. The selectivity of the adsorbent is defined in terms of its ability to separate two components from each other in a mixture (100).

The separation factor, α_{α}, is given as:

$$\alpha_a = \left(X_i / Y_i\right) / \left(Xj / Yj\right) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \qquad (2.1)$$

Here, X_i and Y_i are the equilibrium mole fractions of component i and Xj and Yj are the equilibrium mole fractions of component j, in the adsorbed and fluid phases, respectively. In a particular separation process, the selectivity of an adsorbent becomes noticeable in one or more ways of the following:

[1] **Equilibrium effect**: Differences may exist in the thermodynamic equilibria for each adsorbate-adsorbent interaction which is known as the equilibrium effect.

[2] **Kinetic effect**: Differences may exist in the rates at which different adsorbates travel into the internal structure of the adsorbent and is known as the kinetic effect.

[3] **Molecular sieving effect**: Sometimes pore openings of the adsorbent may be too small to allow penetration by one or more of the adsorbates; this is known as the molecular sieving effect. The molecular sieving effect is an extreme case of the kinetic effect.

[4] **Desorption effect**: When there exists some differences in the rate at which different adsorbates can be desorbed from the adsorbent, the desorption effect takes place.

The equilibrium separation factor depends on:

- The nature of the adsorbent, that is, whether the surface is polar, non-polar, hydrophilic, hydrophobic, etc.,
- The process conditions such as temperature, pressure and concentration.

Kinetic separation is possible only with molecular sieve adsorbents such as zeolites and carbon sieves and it is largely determined by the ratio of micro pore diffusivities of the components being separated. For a useful separation to be based on kinetics, the size of the adsorbent micro pores must be comparable with the dimensions of the diffusing adsorbate molecules. Finally, Table 2.5 lists typical applications of common types of adsorbent.

Table 2.5 Typical applications of commercial adsorbents

Type	Typical applications
Silica Gel	Drying of gases, refrigerants, organic solvents, transformer oils. Desiccant in packings and double glazing. Dew point control of natural gas.
Activated alumina	Drying of gases, organic solvents, transformer oils. Removal of HCI from hydrogen. Removal of fluorine and boron-fluorine compounds in alkylation processes
Carbons	Nitrogen from air. Hydrogen from syn-gas and hydrogenation processes. Ethene from methane and hydrogen. Vinyl chloride monomer (VCM) from air. Removal of odours from gases. Recovery of solvent vapours. Removal of SO_x and NO_x. Purification of helium. Clean-up of nuclear off-gases. Decolourizing of syrups, sugars and molasses. Water purification, including removal of phenol, halogenated compounds, pesticides, caprolactam, chlorine
Zeolites	Oxygen from air. Drying of gases. Removing water from azeotropes. Sweetening sour gases and liquids. Purification of hydrogen. Separation of ammonia and hydrogen. Recovery of carbon dioxide.

	Separation of oxygen and argon. Separation of xylenes and ethyl benzene. Separation of normal from branched paraffins. Purification of nuclear off-gases. Recovery of carbon monoxide from methane and hydrogen. Separation of olefins and aromatics from paraffins. Separation of cresols. Removal of acetylene, propane and butane from air. Drying of refrigerants and organic liquids. Separation of solvent systems. Purification of silanes. Recovery of fructose from corn syrup. Pollution control, including removal of Hg, NO_x and SO_x from gases.
Polymers and resins	Water purification, including removal of phenol, chlorophenols, ketones, alcohols, aromatics, aniline, indene, polynuclear aromatics, nitro- and chlor-aromatics, PCBs, pesticides, antibiotics, detergents, emulsifiers, wetting agents, kraftmill effluents, dyestuffs. Separation of aromatics from aliphatics. Separation of fatty acids from water and toluene. Separation of hydroquinone from monomers. Recovery and purification of proteins, enzymes, steroids, amino acids and polypeptides. Removal of colors from syrups. Removal of organics from hydrogen peroxide Treatment of edible oils. Removal of organic pigments. Refining of mineral oils. Removal of polychlorinated biphenyls (PCBs).
Clays (acid treated and pillared)	Treatment of edible oils, Removal of organic pigments. Refining of mineral oils. Removal of polychlorinated biphenyls (PCBs)

2.9 Adsorption Isotherms

Adsorption is also described via isotherms. The relation between the quantity of adsorbate on the adsorbent and the concentration is known as the adsorption isotherm which can be described by the following equation. There are two conditions to be met: (i) the various reaction equilibrium of retention is reached, and (ii) all the physic-chemical parameters are constant. The word "isotherm" is related to the effect of the temperature on the sorption reaction where the temperature remains constant.

In the previous work by Limousin and his co-researchers (101), it states that when the retention of a solute on solid particles is investigated, the remaining solute concentration of the compound C(mol/L or kg/L) can be compared with the concentration of this compound retained on solid particles Q(mol/kg or kg/kg). In Fig 2.7, the concentration of the compound retained on solid particles Q is calculated by the difference between the initial solute concentration (C_{ao} or C_{bo}) and the final solute concentration C only if the initial solid concentration (Q_{ao} or Q_{bo}) is negligible or previously measured.

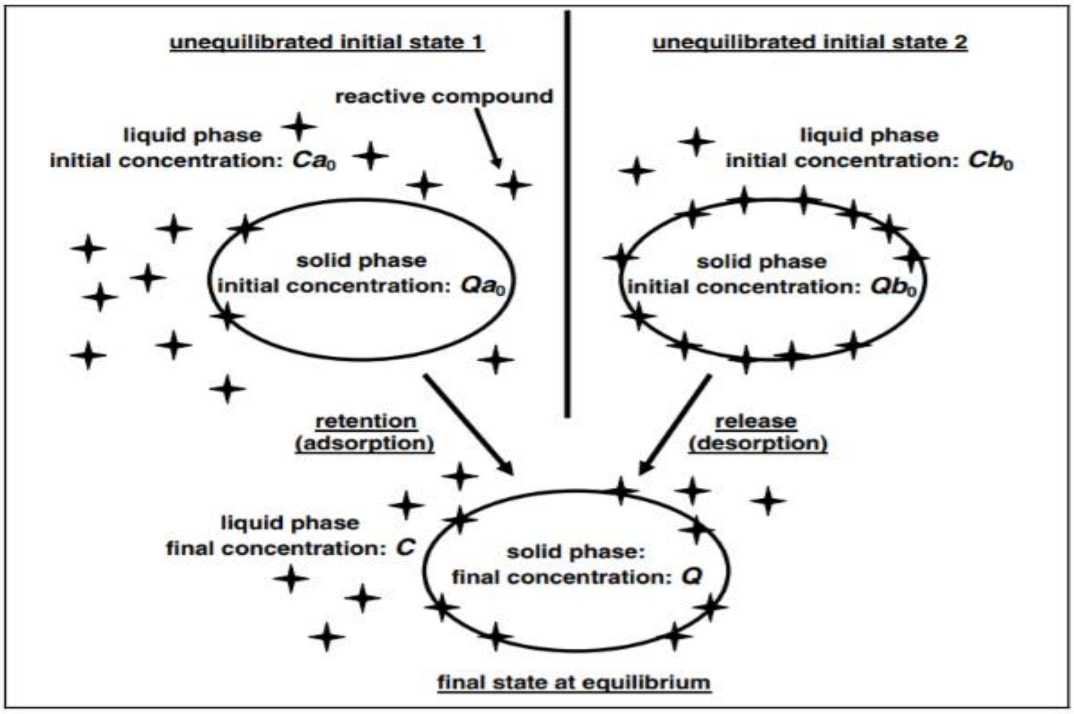


Fig 2.7 Schematic views of the adsorption and desorption phenomena (102)

In the retention stage, the solid concentration at equilibrium Q(mol/kg) is defined in Eq.(2.2),where V is volume of solution (L), m is solid mass (g), C_{ao} is initial solute concentration (mol/L),C is final solute concentration (mol/L)and Q_{ao} is concentration of the compound initially retained on the solid (mol/kg).

$$Q = V/m. \left(C_{ao} - C\right) + Q_{ao} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(2.2)}$$

For the case of a release stage of a compound which is initially retained on the solid phase, the quantity of this initially retained compound Q_{bo} must be measured in advance. Then, the solid concentration at equilibrium can be calculated using equation (1), replacing C_{ao} by C_{bo} and Q_{ao} by Q_{bo} (101).

Adsorption isotherm is important in explaining how solutes interact with adsorbents, thus optimizing the use of adsorbents. In the current development, various types of isotherm models have been developed to describe the process of adsorption. Langmuir and Freundlich isotherms are the two common adsorption isotherms used to explain the equilibrium characteristics of adsorption (102).

2.9.1 The Langmuir isotherm

The Langmuir model (Langmuir, 1918) is the most straightforward non-linear isotherm model, which is based on a few assumptions: (i) the maximum adsorption occurs when there is a saturated monolayer of solute molecules exist on the surface of the adsorbent, (ii) the energy of adsorption on the surface is uniform, and (iii) there is no transfer of adsorbate molecules in the surface plane (103).

The adsorption takes place on localized sites with no lateral adsorbate-adsorbate interactions. Langmuir model can be derived variously by mass action, kinetic, or statistical thermodynamic approaches. The rate at which adsorbate molecules strike a surface of an adsorbent is proportional to the product of the concentration of the solute (C) and the fraction (1-θ) of the surface remaining uncovered by adsorbate and therefore available as adsorption sites. The rate of desorption from the surface is directly proportional to the fractional surface coverage, θ, and the rates of adsorption and desorption are equal at equilibrium. Thus,

$$k_a . C \ (1 - \theta) \ = \ k_d . \theta \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ (2.3)$$

Where k_a and k_d are the rate coefficients for adsorption and desorption respectively. The fractional surface coverage θ, is then,

$$\theta = q_e / q_m = bC_e / \left(1 + bC_e\right) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ (2.4)$$

Where b is k_a/k_d and q_m is the quantity of adsorbate required to form a single monolayer on unit mass of the solid and q_e is the amount adsorbed on unit mass of the solid when the equilibrium concentration is C_e.

The simple derivation assumes that a single molecule occupies a single surface site and that there are no interactions between adjacent adsorbed molecules. Application of the kinetic theory of gases reveals that the constant b can be identified as

Equation (2.4) can be rearranged to the form:

$$q_e = (q_m b\, C_e)/(1 + b\, C_e) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(2.5)}$$

or in the linear form as:

$$C_e / q_e = (1/bq_m) + (1/q_m)\, C_e \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(2.6)}$$

The linear Langmuir plots are obtained by plotting C_e/q_e vs. C_e. The slope and the intercept of this plot give the values of q_m and b. The Langmuir equation is also used to obtain R_L, a dimensionless equilibrium parameter or the separation factor, from the expression:

$$R_L = 1/\ (1 + bC_e) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(2.7)}$$

where C_e is any equilibrium liquid phase concentration of the solute at which adsorption is carried out. The nature of the isotherms is indicated by the R_L value as follows:

R_L value	Type of isotherm
$0 < R_L < 1$	Favorable
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$R_L = 0$	Irreversible

2.9.2 The Freundlich isotherm

There is abundant evidence to show that, for many systems, the heat of adsorption decreases in magnitude with increasing extent of adsorption. If the decline in heat of adsorption is logarithmic, it implies that adsorption sites are distributed exponentially with respect to an adsorption energy which differs between groups of adsorption sites. This is precisely the assumption made by Zeldowitch as early as 1935 in his derivation of a now classic isotherm reflecting the variation in heat of adsorption with coverage. The equation obtained by Zeldowitch is synonymous with the well-known Freundlich isotherm, previously considered to be an empirical isotherm.

The Freundlich isotherm model is an empirical equation for describing the physical adsorption of solutes from liquid to solid surface. There is a multilayer adsorption and there is no limit to the amount adsorbed. In the case of heterogeneous surface energies, Freundlich isotherm is better for adsorption isotherm which is defined as:

$$q_e = K_f C_e^{1/n} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots .. (2.8)$$

where C_e and q_e are the equilibrium concentrations of the solute in the liquid phase and in the solid phase respectively, K_f and 1/n being Freundlich coefficients, representing adsorption capacity and adsorption intensity respectively. When the value is approaching 1, the isotherm is linear and the system has a constant free energy at all adsorbate concentrations. As for a value below 1, it indicates a normal Freundlich isotherm whereby the cooperative adsorption occurs if the value of 1/n is more than 1 (104).

The logarithmic form of the equation (2.8) is more useful for fitting data from batch equilibrium studies, and is given by

$$log\ q_e = log\ K_f + \left(1/n\right)\ log\ C_e \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.9)$$

The values of K_f and n are obtained from intercept and slope of the plots of log q_e vs. log C_e, respectively.

2.9.3 Utility of an adsorption isotherm

The adsorption isotherm provides a number of valuable information (105). Some of them are:

- The absorbability of an adsorbent,
- The amount adsorbed per unit mass or the concentration of the adsorbate on the adsorbent,
- The equilibrium adsorbate concentration indicates the maximum amount that can be removed from solution. This quantity remains unchanged with increasing adsorbent amounts,

- The relative steepness of the isotherm can be equated to the sensitivity of the adsorbent to changes in adsorbate concentration.

On the other hand, the adsorption isotherm has some limitations as given below:

- Isotherms are strictly applicable to equilibrium conditions without any time restriction, and hence if true equilibrium is difficult to ascertain, the applicability of the isotherm will be very much hampered,
- Long-term chemical and biological effects are not accounted for by the isotherm.

2.10 Adsorption Kinetics

The adsorption kinetics normally includes two phases: a rapid removal stage followed by a much slower stage before the equilibrium is established (106).

To arrive at an unambiguous rate law, it is necessary that (i) all the molecular details of the reaction, including the energetics and stereo chemistry, should be known and (ii) the mechanism of the reaction including all the elementary steps should be fairly understood.

The rates at which metal ions are taken up by the adsorbent determine the adsorption kinetics and it directly controls the efficiency of the adsorption process. The transfer of metal ions from the liquid phase to the solid phase can be considered as a reversible reaction with an equilibrium being established between the two phases. A batch adsorption kinetic model was used to analyze the batch adsorption data in order to obtain estimates for the rate constants. The simple way to describe the metal removal by adsorbent is:

$$A^{\wedge} \underset{k_2}{\overset{k_1}{\leftrightharpoons}} B^{\wedge}$$

The rate equation for the above reaction is expressed as:

$$dC_B / dt = -dC_A / dt = k_1\left(C_{A0} - C_{A0}X_A\right) - k_2\left(C_{B0} + C_{A0}X_A\right) \ldots\ldots (2.10)$$

where C_A and C_B are the concentrations of the metal ions in solution and on adsorbent, respectively, at any time; C_{A0} and C_{B0} are the initial concentrations of metal ions in solution and in adsorbent, respectively (at t=0); X_A is the fraction of metal adsorbed onto the adsorbent; k_1 and k_2 are the first-order adsorption and desorption rate coefficients, respectively. At equilibrium:

$$dC_B / dt = - dC_A / dt = 0 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(2.11)}$$

and,

$$X_{Ae} = \left[k_c - \left(C_{B0} / C_{A0}\right)\right] / \left(1 + k_c\right) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(2.12)}$$

where X_{Ae} is the fraction of the metal ions adsorbed at equilibrium, and k_c is the equilibrium constant.

The equilibrium constant, K_c is represented as:

$$K_c = k_1 / k_2 = \left(C_{B0} + C_{A0} X_{Ae}\right) / \left(C_{A0} - C_{A0} X_{Ae}\right) \ldots\ldots\ldots\ldots\ldots\ldots\text{(2.13)}$$

The equation (2.10) can be written as:

$$dX_A / dt = \left(k_1 + k_2\right)\left(X_{Ae} - X_A\right) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(2.14)}$$

Substituting (k_1/K_c) for k_2, the integrated form of the equation (2.14) can be written as:

$$-ln\left(1 - X_A / X_{Ae}\right) = \left(k_1 + k_1 / K_c\right) t \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(2.15)}$$

or

$$, -ln\left(1 - X_A / X_{Ae}\right) = -k' t \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(2.16)}$$

where, k´ is the overall rate coefficient and is given by,

$$k' = k_1 + k_1 / K_{c\,=} k_1 + k_2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(2.17)}$$

In most cases, however, the adsorption kinetics can be best described by adopting well known simple models and by trying to fit the experimental data into them. A few established models for adsorption kinetics are:

2.10.1 Lagergren pseudo first order kinetics.

The Lagergren equation (107) has been one of the most used equations particularly for pseudo first order kinetics:

$$dq_t / dt = k_1 (q_e - q_t) \text{..} (2.18)$$

where $k_1(min^{-1})$ is the pseudo first order adsorption rate coefficient. The integrated form of the equation (2.18) for the boundary conditions of t = 0, $q_t = 0$ and t = t, $q_t = q_t$, is

$$ln(q_e - q_t) = lnq_e - k_1 t \text{..} (2.19)$$

where q_e and q_t are the values of the amount adsorbed per unit mass at equilibrium and at any time t. The values of k_1 can be obtained from the slope of the linear plot of ln (q_e-q_t) vs. t.

An important test for the validity of the pseudo-first order kinetics is to compare q_e obtained from the intercept (ln q_e) of the plots of ln (q_e-q_t) vs. t with the value obtained experimentally when the adsorption reaches equilibrium. In most cases, the Lagergren equation does not fit well in the whole range of interaction time and then, another suitable model will have to be looked for.

2.10.2 Pseudo-second order equation.

When the applicability of the first order kinetics becomes untenable (for example, if q_e obtained on the basis of equation (2.19) is not the same as the one obtained experimentally), the adsorption may follow second order kinetics on the basis of the equation (107, 108):

$$dq_t / dt = k_2 (q_e - q_t)^2 \text{ ....} (2.20)$$

where k_2 is the second order rate coefficient. The integrated form of the equation (2.20) under the boundary conditions of $q_t = 0$ at t = 0 and $q_t = q_t$ at t = t is given by,

$$q_t = t / \left[\left(1 / k_2 q_e^2\right) + t / q_e \right] \text{..................................} (2.21)$$

The linear form of this equation

$$t/q_t = 1/\left(k_2 q_e^{\,2}\right) + \left(1/q_e\right).t \text{ ………………………………… (2.22)}$$

makes it possible to obtain q_e and k_2 (g mg^{-1}min^{-1}) from the plots of t/q_t vs. t.

2.10.3 Elovich equation.

The Elovich equation assumes that the actual solid surfaces are energetically heterogeneous. Such assumption seems obvious because neither desorption nor interactions between the adsorbed molecules could substantially affect the kinetics of adsorption at low surface coverage. The crucial effect of the surface energetic heterogeneity on the equilibria of adsorption in the gas/solid systems has been demonstrated by Rudzinski and Everett (1992). The Elovich Equation (109) has been used in the form:

$$dq_t / dt = \alpha \; exp\left(-\beta \; q_t\right) \text{………………………………….. (2.23)}$$

Assuming $\alpha\beta t >> 1$, and $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, the linear form of the equation (2.23) is given (110):

$$q_t = 1/\beta \; ln \; \left(\alpha\beta\right) \; + 1/\beta \; ln \; t \text{ ……………………………… (2.24)}$$

Where α and β, known as the Elovich coefficients, represent the initial adsorption rate (g mg^{-1}min^{-2}) and the desorption coefficient (mg g^{-1}min^{-1}) respectively. The Elovich coefficients could be computed from the plots of q_t vs. ln t.

2.10.4 Intra particle diffusion.

For porous adsorbents, the diffusion of the adsorbate molecules or ions into the pores has also to be taken into account in finding a suitable kinetic model for the process. In many cases, the intra particle diffusion may control the rate of uptake of an adsorbate, which is represented by the following expression: (111)

$$X_A / X_{Ae} = 1 - \left(6/\pi^2\right) \; \Sigma \; \left(1/n^2\right) \; exp \; \left(-n^2\pi^2 D_c t / r^2\right) \text{………... (2.25)}$$

where X_A is the amount of the adsorbate (A) adsorbed at any time and X_{Ae} the amount adsorbed at equilibrium, their ratio giving the fractional approach to equilibrium, D_c= intra-crystalline diffusivity, r= particle radius, t= reaction time, and the summation is carried out from n=1 to n=α.

The equation (2.25) can be rewritten in the following simplified form:

$$1 - X_A / X_{Ae} = \left(6/\ \pi^2\right) exp\ \left(-\pi^2 D_c / r^2\right)\ t \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. \ (2.26)$$

or, $$ln\ \left(1 - \ X_A /\ X_{Ae}\right) = \left(-\pi^2 D_c / r^2\right)\ t\ +\ ln\ \left(6/\pi^2\right) \ldots\ldots\ldots \ (2.27)$$

Therefore, the plot of $ln\ \left(1 - X_A /\ X_{Ae}\right)$ versus t should be linear with a slope of $\left(-\pi^2 D_c / r^2\right)$, which is known as the reaction rate constant or diffusion time constant. The slope can be expressed as:

$$k' = \pi^2 D_c / r^2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ (2.28)$$

where k´ is the overall rate constant, inversely proportional to the square of the particle radius.

Weber and Morris (1963) (112) introduced a simpler expression to obtain the diffusion rate coefficient, k_i:

$$q_t =\ k_i . t^{0.5} + C_i \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ (2.29)$$

k_i (mg g^{-1} $min^{-1(1/2)}$)) is a measure of diffusion coefficient. C_i = intraparticle diffusion constant i.e. intercept of the line (mg g^{-1}). It is directly proportional to the boundary layer thickness.

The significant feature of this expression is that the linear plots of q_t vs. $t^{0.5}$ should pass through the origin (zero intercept). Thus the intra-particle diffusion model can be easily tested through the above plots provided they have zero intercept, which indicates a controlling influence for the diffusion process on the kinetics. The rate coefficient, k_i (mg g^{-1} $min^{-0.5}$) could be obtained from the slope of the plots.

2.10.5 Liquid film diffusion.

When the flow of the reactant from the bulk liquid to the surface of the adsorbent is the slowest process determining kinetics of the rate processes, the liquid film diffusion model (113) given by the simple relation

$$ln\ (1-F) = -k_{fd}t \qquad (2.30)$$

could be the appropriate way to characterize the kinetics. F is the fractional attainment of equilibrium $(= q_t / q_e)$ and k_{fd} (min^{-1}) is the adsorption rate coefficient. A linear plot of $-ln\ (1-F)$ vs. t with zero intercept suggests that the kinetics of the adsorption process is controlled by diffusion through the liquid film surrounding the solid adsorbent.

2.11 Thermodynamics of adsorption

The phenomenon of adsorption is essentially an attraction of adsorbate molecules to an adsorbent surface. It is important to estimate the strength of binding of species to a surface. When an isolated species approaches the surface of a solid, several interactions come into play, each of which contributes to the heat or energy of physical adsorption (114). Physical adsorption has always been found to be an exothermic process accompanied by release of heat as the adsorbate molecules accumulate on the adsorbent surface due to weak binding forces such as van der Waals forces. The exothermic nature of the process is supported by the facts that (i) physical adsorption is a spontaneous process accompanied by a decrease in Gibbs energy ($\Delta G < 0$), and (ii) since the adsorbate molecule lose at least one degree of freedom, the process is also accompanied by a decrease in entropy ($\Delta S < 0$). Therefore, it follows from the basic thermodynamic relation, $\Delta G = \Delta H - T\Delta S$, that with both $\Delta G, \Delta S < 0$, the enthalpy change, ΔH also decreases, i.e. $\Delta H < 0$. The Gibbs free energy, enthalpy and entropy (ΔG, ΔH, ΔS), for the adsorption process are obtained from the experiments carried out at different temperatures.

In physical adsorption, weak forces are involved. These may be van der Waals type, dipole-dipole interactions, hydrogen bonding, etc. With chemisorption, the forces involved are strong and chemical in nature leading to formation of surface compounds and the mechanism of adsorption will be vastly different from that of physical adsorption. While the heat measured for physical adsorption corresponds to the normal crystallization enthalpies, the chemisorption heat is at least an order of magnitude higher. It is also possible that both physical and chemical adsorption take place simultaneously and in such cases, the actual mechanism will be a combination of both the processes. The thermodynamics of an adsorbate-adsorbent system therefore depends on various factors, viz., (i) chemical nature of the adsorbate and (ii) the adsorbent, the environmental conditions such as pH in case of adsorption from solution, and (iii) the type of forces interacting. Physical adsorption is normally characterized by enthalpy change of 10 to 40 kJ mol^{-1}.

The thermodynamic parameters for the adsorption process, ΔH (kJ mol^{-1}), ΔS (J K^{-1} mol^{-1}) and ΔG (kJ mol^{-1}), are evaluated using the equations (2.31) and (2.32) (100):

$$\Delta G = -RT \; ln \; K_d \; \ldots\ldots\ldots\ldots\ldots\ldots \; (2.31)$$

$$ln \; K_d = -\Delta G / RT = \Delta S / R - \Delta H / RT \; \ldots\ldots\ldots\ldots\ldots\ldots \; (2.32)$$

where, K_d = the distribution coefficient of the adsorbate, (= q_e/C_e in L g^{-1}),
T = the temperature (K),

R = universal gas constant (8.314×10^{-3} kJ K^{-1} mol^{-1}).

The plot of ln K_d vs. 1/T should be linear with the slope $(-\Delta H / R)$ and the intercept $(-\Delta S / R)$ giving the values of ΔH and ΔS. The Gibbs energy change, ΔG, is the fundamental criterion of spontaneity. Processes occur spontaneously at a given temperature if ΔG is a negative quantity. All these relations are valid when the enthalpy change remains constant in the range of temperatures considered.

2.12 Desorption and Regeneration of the Adsorbent

In certain applications it may be economic to discard the adsorbent after use in which case it may be necessary to describe it as a waste. Disposal would be favored when the adsorbent is of low cost, is very difficult to regenerate (due to chemical forces) and the non-adsorbed products of the adsorptive separation are of very high value.

However, the disposal of the adsorbent as a waste is not considered as an economic option, and regeneration should be considered as an option. For this, desorption and regeneration is to be carried out with one or more of the following:

(i) Increase in temperature;
(ii) Reduction in partial pressure;
(iii) Reduction in concentration;
(iv) Removal with an inert fluid;
(v) Displacement with a more strongly adsorbing species;
(vi) Change of chemical condition such as pH.

Chapter Three

Experimental Work

3.1. Apparatus

- Different glasses and flasks
- Filter papers
- Hot plate
- Laboratory oven
- Laboratory photometer (Clin Check Plus)
- Laboratory Centrifuge
- Burning furnace
- Electronic balance
- Pounder and different size of sieves
- Orbital compact shaker
- PH-meter Instrument
- Sieve 75 µm

3.2. Materials

Methyl orange dye (MO), (4-[[(4-Dimethylamino) phenyl] azo] benzene sulfonic acid sodium salt, C.I. 13025, MW=327.34 g/mole, dye content 85%) was obtained from chemical laboratory.

H_2SO_4 and NaOH (for initial pH adjustment), were obtained from chemical laboratory.

Raw anthracite (An) and Chitosan (Cs) were brought from the Holding Company for water and wastewater.

3.3. Experimental methods

3.3.1 Preparation of Modified Seaweed (MS)

Marine seaweed (S) was collected from the coastal area of Zliten, Libya. The seagrass was identified as (Posidonia oceanica). It was repeatedly washed several times with tap water followed by distilled and dried at room temperature, then was cut with a scissors into irregular shaped particles between

5 and 10 mm in size, filtered and finally dried in oven at 105^0C for 2hr. The dry sample activated by a solution of 10% sulpheric acid H_2SO_4 for 24h (solid/liquid ratio of 1/6), Every 10 g of dry powdered sample was immersed with 60 mL of sulpheric acid to increase the adsorption capacity of the sorbent material, and stirred on hot plate at 90^0C for 24hr.

The samples were then washed with distilled water several times until the pH of washing water becomes neutral (7), dried in oven at 105°C for 3hr, then burned in burning furnace at 650°C for 2hr.

The residue was crushed, powdered, ground to small particles in an agate mortar, and sieved by using a 75 µ mesh standard sieve to obtain fine powder, finally the resulting material was stored in a glass bottle used for adsorption experiment pretreatment.

3.3.2 Preparation of Chitosan (Cs) solution

0.5 g of chitosan was dissolved in 100 ml of acetic acid 2%, stirred on magnetic stirrer at 80°C for 2hr; we obtained a high viscosity solution.

3.3.3 Preparation of MS/Cs/An composite

2 g of the MS was homogeneously mixed with 0.5 g of An (solid/solid ratio of 4/1). Then dissolved in 10 ml of Cs solution, stirred, and heated at 70°C for 24hr. This minute quantity of An was selected to achieve the planned goal with minimal costs. The calcinated mixture was gently ground and stored for further application under the name of MS/Cs/An composite.

3.3.4 Preparation of dye solution (Adsorbate solution)

Methyl Orange dye MO ($C_{14}H_{14}N_3SO_3Na$) with a purity of 90%, average molecular weight was 927.02. A 2000 ppm solution of methyl orange dye was prepared by weighing accurately 1 gram of dye was dissolved in 500 ml standard flask, it was made up to the mark with deionized water of distilled water, to prepare a stock solution of the dye.

The stock solution was diluted with deionized water to obtain different dye concentrations (30, 40, 50, 60, and 70 ppm).

3.3.5 Preparation of chemical regents

Grade reagents were used in this study of analytical grade; reagent grade diluted H_2SO_4, NaOH and pH buffer solutions were used to adjusted pH values of samples. In all experimental work, double distilled water was used.

3.3.6 Materials characterization

MS and MS/Cs/An composite were characterized using different analytical techniques such as; X–ray diffraction model Philips APD–3720 diffracto meter and FTIR; Whereas, the morphological features were investigated by a Scanning electron microscopy (SEM, JSM-6700 F, JEOL, Japan); DSC (TA Instruments Q2000 DSC); TGA (Q500 equipment thermo gravimetric analyzer); as well as S_{BET} using N_2 adsorption/desorption at 77 K which was conducted using a gas sorption analyzer (Quantachrome, NOVA, version 11.04, USA), the total pore volume (V_{total}) was estimated from the amount of the adsorbed N_2 gas at P/P_0.

The surface area, pore volume and pore size of both raw MS and the MS/Cs/An composite were determined by a surface area analyzer (Tristar II analyzer) degassing at 200 ^{0}C for 1 hr. The Brunauer–Emmet–Teller17 and Barrett–Joyner–Halenda18 equations were used to estimate the BET surface area (S_{BET}), pore volume and pore size of both Ms and MS/Cs/An, respectively.

3.3.7 Batch adsorption experimental analysis

The adsorption of MO dye on the composite was studied by batch technique, Variation weights of were weighed and mixed into 25 mL of definite concentration of MO solution (50 ppm). The best weight at high adsorption capacity was 35 mg. A certain weight (35 mg) of MS/Cs/An composite and initial dye concentration 30–70 ppm at different agitation rates 50–250 rpm for 5–150 min using an orbital compact shaker (Edmund Buhler, Germany) was studied. The MO solution was separated from the adsorbent by centrifugation at 4,000 rpm using a centrifuge, (Hamilton, Germany), for 10 min. The MO concentrations in the supernatant were estimated using photometer (Clin Check Plus, Italy) at wavelength 468 nm according to (33). The affecting factors can be summarized in Table 3.1. Each sample was examined in triplicate at ambient temperature and the average result was listed.

The effects of some parameters, such as pH, temperatures, concentrations, contact time and dose on the adsorption was studied. The pH of the adsorptive solutions was adjusted using hydrochloric acid, sodium hydroxide and buffer solutions when required. The results of these studies were used to obtain the optimum conditions for maximum dye removal from aqueous solution.

Eqs. (3.1) and (3.2) were applied to estimate the removal percentage and the uptake capacity (mg/g), respectively, where C_0 (mg/L) is the initial concentration of MO and C_e (mg/L) is the equilibrium concentration of MO in solution, V is the volume in L and M is the adsorbent mass (g).

$$\text{Removal \%} = \frac{C_o - C_e}{C_o} \times 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(3.1)}$$

$$qe = \frac{(C_{o-}C_e)V}{M} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(3.2)}$$

Table 3.1 Affecting factors of M.O onto MS/Cs/An composite.

Investigated parameter	**Conditions**								**The other parameters**
pH	2	3^a	4	5	7	9			50 ppm of MO initial conc., 35 mg dose, 200 rpm/2hr (agitation speed/time)

Dose (mg)	5	10	20	30	35[a]	40	50		pH (3.0), 50 ppm of MO initial conc., 200 rpm, 2hr (agitation speed/time)
Agitation time (min)	5	10	15	30	60	90	120[a]	150	pH (3.0), 50 ppm of MO initial conc., 35mg dose, 200 rpm agitation speed
MO initial conc., (ppm)	20	30	40	50[a]	60	70	80		pH (3.0), 35 mg dose, 200 rpm, 2hr (agitation speed/time)
Agitation speed (rpm)	50	100	150	200[a]	250				pH (3.0), 50 ppm of MO initial conc., 35 mg dose, 2hr of agitation
Temp (K^0)	293[a]	303	313	323	333				pH (3.0), 50 ppm of MO initial conc., 35 mg dose, 200 rpm, 2hr (agitation speed/time)

[a] Optimum conditions

3.3.8 Isothermal and kinetic investigation of MO onto MS/Cs/An composite

Langmuir, Temkin, and Freundlich isotherms were applied to evaluate the MO adsorption mechanism onto MS/Cs/An composite adsorbent Table 3.2. As well as kinetic sorption models, Lagergren's pseudo-first-order model (34), pseudo-second-order model, and Intra-particle diffusion Table 3.3.

Table 3.2 Adsorption isotherm models for MO uptake by MS/Cs/An composite

Isotherm Model	Linear form	Parameters	Refs.
Langmuir	$\frac{C_e}{q_e} = \frac{1}{q_{max}\, b} + \frac{C_e}{q_{max}}$ $R_L = 1/\ (1 + bC_0)$ $R_L > 1$ (unfavorable adsorption) $R_L = 1$ (linear adsorption) ($0 < RL < 1$ (favorable adsorption) $R_L = 0$ (irreversible adsorption)	C_e (mg/L): equilibrium concentration of the resting MO in the solution q_e (mg/g): removed amount of (MO) at equilibrium. q_{max} (mg/g): maximum adsorption capacity. b (L/mg): Langmuir constant q_{max}= 1/slope b= slope/ intercept C_0: Initial MO concentration. R_L: Equilibrium parameter of Langmuir equation.	(Langmuir, 1916) Equation (3.3)

Freundlich	$\log q_e = \log K_F + \frac{1}{n} \log C_e$	C_e (mg/L): equilibrium concentration of the resting MO in the solution q_e (mg/g): removed amount of MO at equilibrium. K_F (mg/g): MO adsorption capacity. n: heterogeneity factor. $k_F = 10^{intercept}$ 1/n= slope	(Freundlich, 1906) Equation (3.4)
Temkin	qe = B ln A + B ln Ce B=RT/b	A (L/g): Temkin isotherm constant (the equilibrium binding constant corresponding to the maximum binding energy) B (J/mol): Temkin constant related to heat of sorption. b: Temkin isotherm constant R: The gas constant (8.314 J/mol K) T : the absolute temperature at 298 K $A= EXP^{(intercept/slope)}$ B= slope	(Temkin and Pyzhev, 1940) Equation (3.5)

Table 3.3 Sorption kinetics models for MO uptake by MS/Cs/An composite

Kinetic Model	Linear form	Parameters	Refs.
Pseudo- first order	$\ln (q_e - q_t) = \ln q_e - k_1 t$	q_t (mg/g): removed amount of MO at time t q_e (mg/g): equilibrium adsorption uptake k_1 (g/mg min): rate constant of the first-order adsorption K_1: -slope $q_e^{(calc.)}$: $EXP^{(intercept)}$	(Langergren, 1898) Equation (3.6)
Pseudo-second order	$\frac{t}{q_t} = \frac{1}{k_2\text{-}\, q_e^2} + \frac{t}{q_e}$	q_t (mg/g): removed amount of MO at time t q_e (mg/g): equilibrium adsorption uptake k_2 (g/mg min): rate constant of the second-order adsorption $q_e^{(calc.)}$= 1/slope $k_2 = (slope)^2/intercept$	(Ho and McKay, 1999) Equation (3.7)
Intra-particle diffusion	$q_t = k_p\, t^{1/2} + C$	q_t (mg/g): removed amount of MO at time t. K_p (mg/g $min^{0.5}$): intra-particle diffusion rate constant. C (mg/g): intercept of the line which reflects the thickness of the boundary layer. k_p= slope C= intercept	(Weber and Morris, 1963) Equation (3.8)

3.3.9 Estimation of thermodynamic parameters

Thermodynamic parameters such as Gibb's free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) changes can be determined by the Eqs. (3.9) – (3.10) as shown in Table 3.4 (37):

Table 3.4 Sorption thermodynamic models for MO uptake by MS/Cs/An composite

Kinetic Model	Linear form	Parameters	Refs.
Adsorption thermodynamic	$ln\frac{q_e}{c_e} = \frac{\Delta H}{RT} + \frac{\Delta S}{R}$	(ΔH) j.mol :enthalpy change (ΔS) j.mol: entropy change R gas constant 8.314 $J\cdot K^{-1}\cdot mol^{-1}$ q_e (mg/g): equilibrium adsorption uptake C_e (mg/l): concentration of MO	(Van't Hoff's equation 1887) Equation (3.9)
	$\ln(Kexp) = \ln(A) - \frac{Ea}{RT}$	*k* is the rate constant *T* is the absolute temperature in Kelvin *A* is the frequency of collisions in the correct orientation, E_a is the activation energy (KJ) R gas constant 8.314 $J\cdot K^{-1}\cdot mol^{-1}$	Arrhenius(1898) Equation (10)

Chapter Four

Results and Discussion

4.1 Characterization of MS/Cs/An composite

4.1.1 Identification of MS and MS/Cs/An composite

The X–ray diffraction paradigm of the raw (MS) confirmed that graphite is the main crystalline phase at 2θ 25°, 32°, and 46°, Figure (4.1 A). The strong peak at 24.2° is related to the reflection of silicon dioxide (115). The strong diffraction at 25° may be attributed to the crystalline carbon in MS samples.

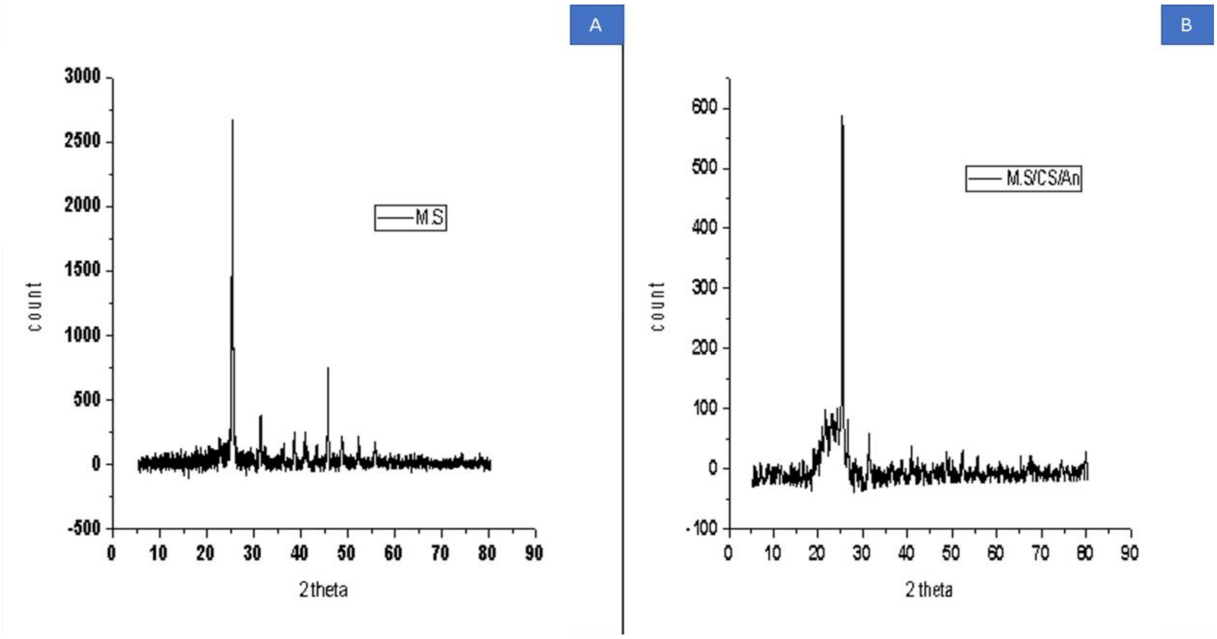


Fig 4.1 XRD pattern of MS (A) and MS/Cs/An composite (B).

Figure (4.1 B) The X–ray diffraction data of the MS/Cs/An also confirmed the same diffraction peak, but it is slightly shifted to the right with stronger intensity than MS, these results are compatible with the reported conclusions of (116). The presence of the amorphous graphite structure of (MS/Cs/An) was indicated by a sharp peak at θ 26.1°. On the other hand, another one appeared at θ 23.2°, whereas, graphite peak appeared at θ 31.8° as a weak peak (117,118) taking into consideration the random layer lattice structure of anthracite (119,120).

4.1.2 Thermal characterization

The thermal stabilities of the nanocomposite were evaluated by TGA (TA Instruments Q500 equipment thermogravimetric analyzer). Samples were heated at nitrogen purge flow 50 mL/min at 25°C–900°C at a heating rate of 10°C/min. The glass transition of the polymer was further studied by differential scanning calorimetry (TA Instruments Q2000 DSC). The thermal history of the samples was erased by heating from 25°C–350°C at a heating rate of 10°C/min and a nitrogen purge flow of 50 mL/min.

Figure (4.2) was presented the TGA Thermogram of the MS and MS/Cs/An composite samples displaying two stages of weight loss at different temperature range, the first stage of weight loss was 0.5 and 0.2 mg respectively, at 100 and 120°C, respectively, may be due to the release of volatile gases such as CO, CO_2, and SO_2. Generally, the weight loss below 100°C attributed for hygroscopic water (121,122). The 2nd stage of weight loss of 4 and 1.5 mg was detected at 500°C and 570°C, respectively. The decrease of weight loss with rising the temperature is attributed to the decomposition of chitosan removal of volatile organic materials. At 100°C the weight loss was 0.5 and 0.2 mg for MS and MS/Cs/An, respectively. On the other hand, the weight loss was 4 and 1.5 mg at 550°C for MS and MS/Cs/An, respectively, this due to evaporation of gases from MS and MS/Cs/An.

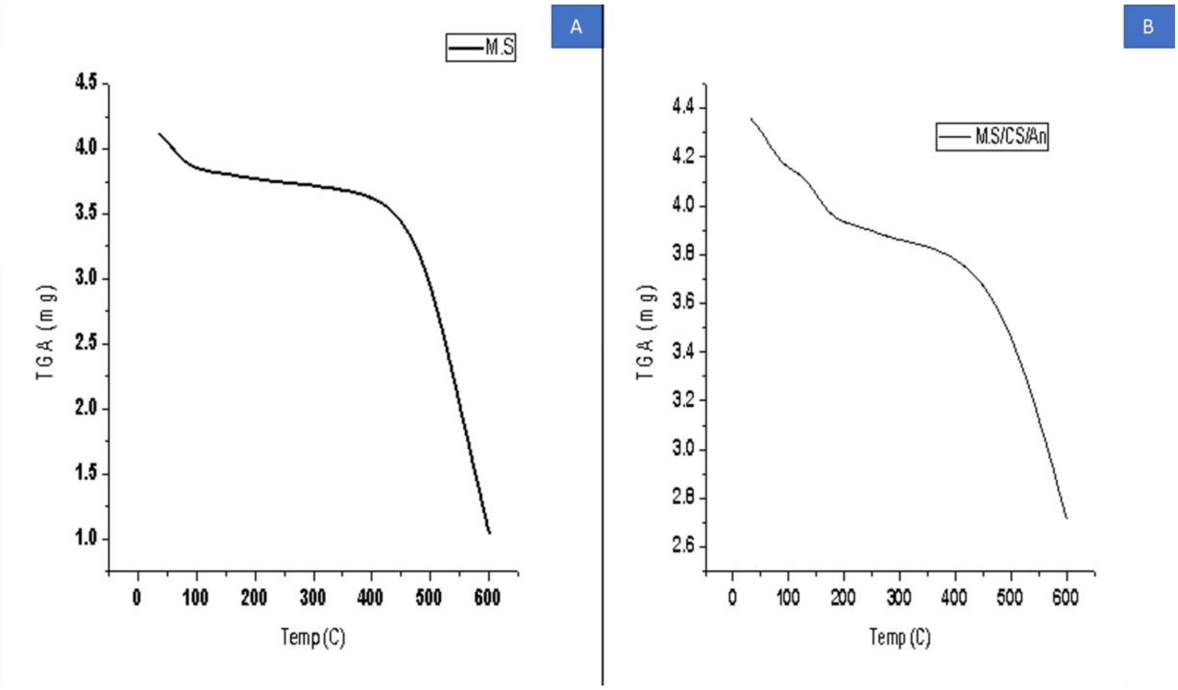


Fig 4.2 TGA Thermogram of MS (A) and MS/Cs/An (B) composite.

Figure (4.3) illustrates the DSC Thermogram of MS and *MS/Cs/An composite* which indicates that the volatile gases and volatile materials were lost around 80°C, while a small amount of these gases were lost at 50°C. Because of the release of the organic materials and the volatile gases from (MS) and (*MS/Cs/An composite*), DSC Thermogram showed an endothermic behavior in the case of MS and endothermic/exothermic in the case of *MS/Cs/An composite*.

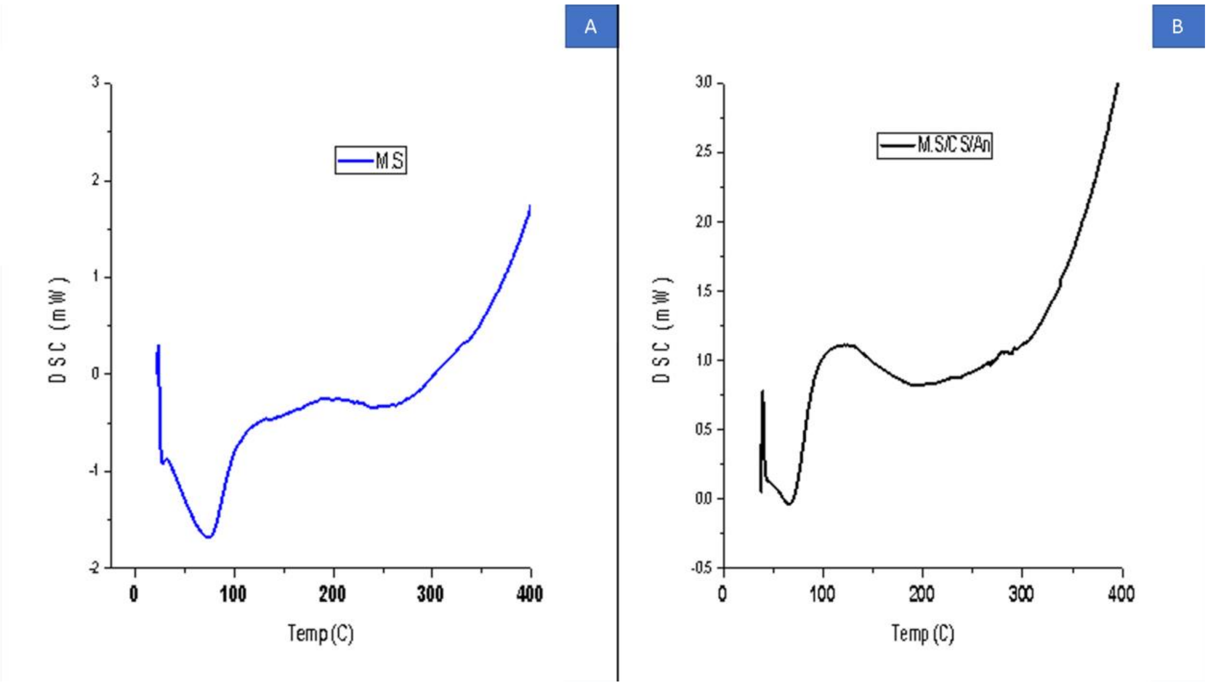


Fig 4.3 DSC Thermogram of MS (A) and MS/Cs/An (B) composite.

4.1.3 Fourier transform infrared spectroscopy characterization

The FTIR spectrum of MS and MS/Cs/An composite (Fig 4.4 A and B) showed the characteristic broad band's at C=C stretching, Si–O–Si, Al–O–Si and C-O bending, located at 1660, 1081, 877 and 718 cm^{-1}, respectively (123;124,125), peak at 576 cm^{-1} which ,corresponding to Fe-O (123) in addition to the peaks of amide group of chitosan at 1565 cm^{-1} as a weak band (126;127), cross linking agent of C=N stretching, this observed peak confirms the strong binding of chitosan (128;129). The peak at~ 870 cm^{-1} related to C-H wagging of the saccharide structure of chitosan (130). The bands at 3,479 and 3,410 cm^{-1} are assigned to the coupled OH stretching mode

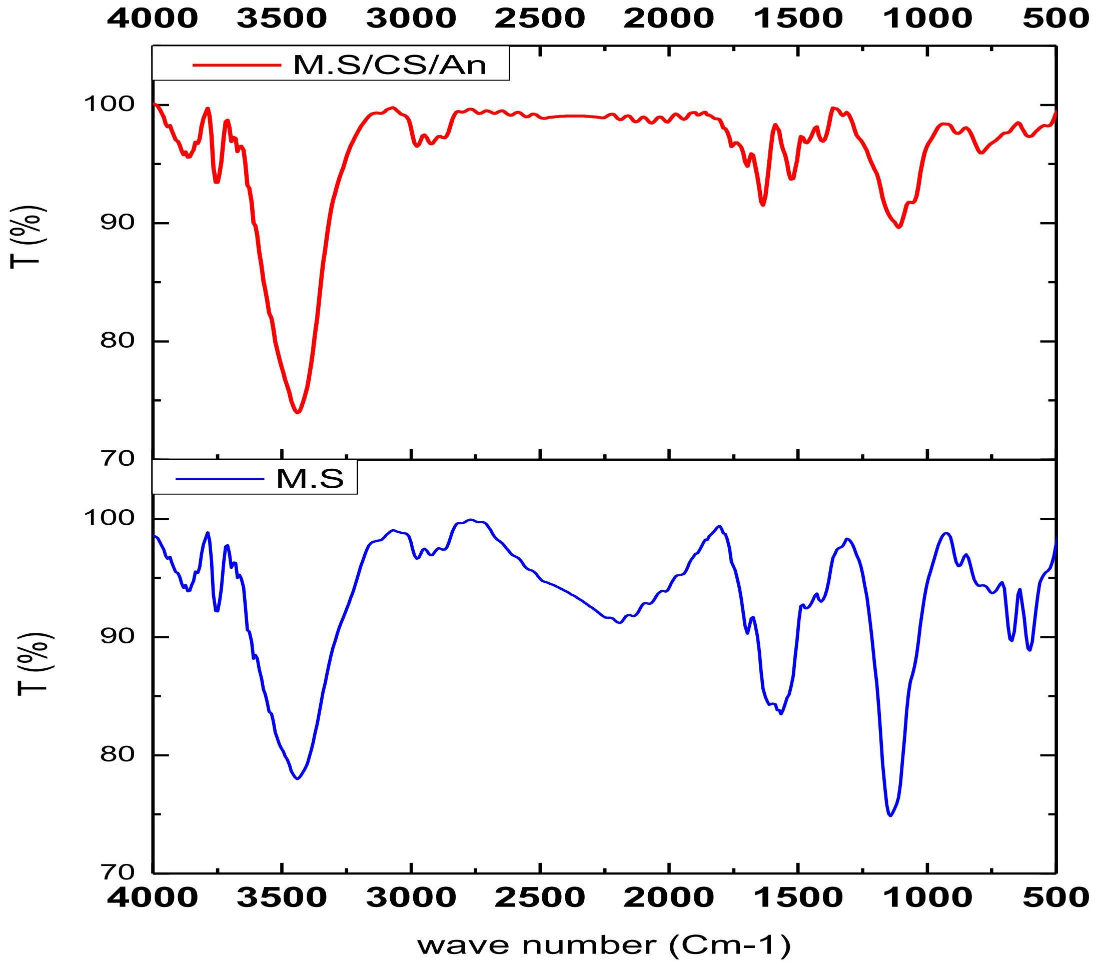


Fig 4.4 FTIR Pattern of MS and MS/Cs/An composite.

4.1.4 Surface Morphology and elemental analysis

The SEM photographs confirmed the porous and flaky nature of (MAn) with a conspicuous variance in its grain sizes and shapes, Figure 4.5. Also the appearance of the hexagonal crystals of graphite complies with the XRD results.

The elemental analysis was carried out using the SEM micrograph in MS and MS/Cs/An shown in Figure 4.5 (A-B), respectively. Inhomogeneous topography of minerals trapped in a carbon matrix was identified by surface morphology. On the other hand, the incorporation of MS/An into Cs polymer showed bright and opaque features in MS/Cs/An composite. In MS and MS/Cs/An composites, SiO_2 and Al_2O_3 have been identified as large particles measuring 10 µm in size. Increasing in oxygen content and decreasing in carbon content of the MS/Cs/An composite sample may be attributed to the addition of anthracite and chitosan of the composite MS/Cs/An, there are small particles mixed on the surface of the MS, fine lines and ultimately seen in porous form due to binding with anthracite and chitosan.

Increasing in MS/Cs/An composite holes contributes to an increase in the surface area (245 to 314 m^2/g), which occurred after mixing with anthracite and chitosan at temperatures of 70 and 90°C during the preparation and treatment of MS/Cs/An composites. At these temperatures, volatile gases containing CO, CO_2, and H_2 gases are evaporated, leaving these voids (131).

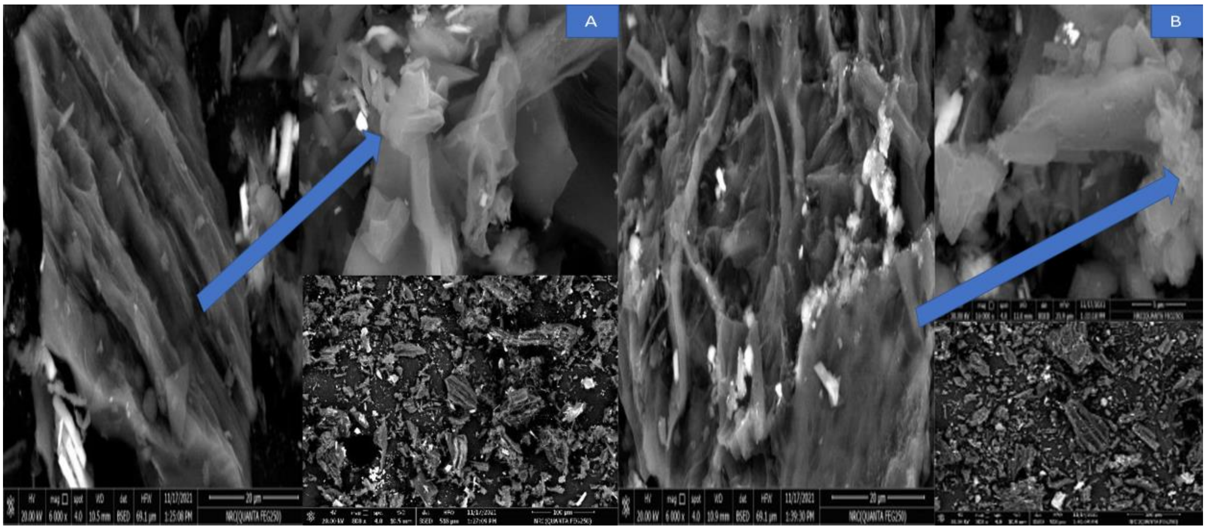


Fig 4.5 SEM micrograph of MS (A) and MS/Cs/An (B) composite.

4.1.5 N_2 Adsorption analysis

N_2 adsorption / desorption isotherms obtained at 77 K and BJH pore size distributions of MS/An/CS composite distributions are shown in Fig 4.6 (A, B). The results of the MS/An/CS composite based on BET analysis show the adsorption-desorption isotherms are compatible of Type I curves according to the IUPAC classification, which is an indicator of the presence of a narrow mesopore micro-porosity structure and a wider structure of micropores. The specific surface area (SSA) of the composite MS/An/CS increased significantly from 245.1 m^2/g to 314.5 m^2/g, due to impregnation of anthracite which has a high specific surface area, suggesting a high concentration of micropores in the composite MS/An/CS (132), with micropores gradually rising from 0.800998 to 0.928484 (cm^3/g). Subsequently, during the preparation and curing of the MS/An/CS composite, low-density volatile gases were escaped after the heat treatment of the MS/An/CS composite, suggesting a tidy formation, resulting in a shrinking hole between the layers. The pore curing will therefore extend the pore volumes and develop the SSA and the highly microporous structure of the composite MS/An/CS dramatically.

In addition, the pore size distributions measured by the BJH of the composite MS/An/CS are shown in Fig 4.6 B. As shown in the figure, the small pore diameter distribution of the composite MS/An/CS is 1.5-5 nm with large pores varying from 5 nm to more than 50 nm.

The results show that the degree of microcrystalline MS structure shifts significantly and increases the degree of graphitization due to high temperature and increased degree of carbonization, which may result in good sorptive material (133). However, average pore size, surface area and total pore volume obtained from MS/An/CS composite derived from MS are 5.09314 nm, 314.5 m^2/g and 0.800998 cm^3/g, respectively (Table 4.1).

Table 4.1: Textural parameters of MS and MS/An/CS composite.

Specimen	S_{BET} (m^2/g)	Pore Size (Vt) (cm^3/g)	The Mean Pore width (nm)
MS	245.1	0.928484	7.57641
MS/An/CS	314.5	0.800998	5.09314

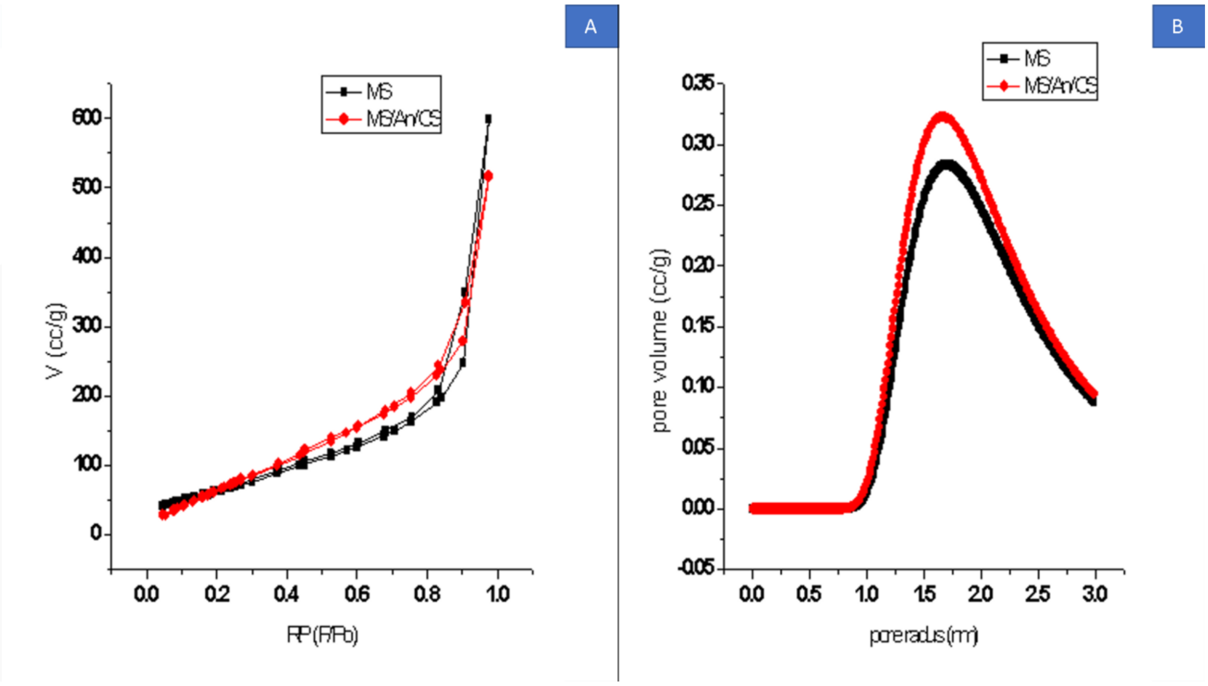


Fig 4.6 N_2 adsorption/desorption isotherms curves of MS and MS/An/CS composite obtained from the nitrogen gas.

4.2 Factors affecting the adsorption process:

4.2.1 Effect of pH

The adsorption of MO by MS/Cs/An composite is a pH-dependent process. The results indicated that the removal percent (R %) of MO was very high at low pH values as demonstrated in Table 4.2 and Fig. 4.7a, and the maximum removal efficiency (98%) was achieved at pH 3.0. Therefore, the pH=3 was selected as the optimum pH and applied for all the adsorption studies to verify equilibrium accomplishment.

The slight decrease in its geometrical parameters could be related to its higher degree of graphitization. Beyond pH 4.0, MO sorption was noticeably declined, especially under basic conditions. This coincides with the point of zero charge (pH_{PZC}) determined according to the reported protocol.

The higher degree of ionization of MO (pKa=3.46) and the protonation of the MS/Cs/An composite surfaces at pH 3.0, promoted the electrostatic interactions between the binding sites of the studied sorbents (protonated hydroxyl groups) and the negative sulfonate group ($–SO_3^-$) of MO ions in solution. In the protonation process of the MS/Cs/An composite surfaces, hydrogen ions act as bridging ligands between the MO anions and the surface of the studied sorbents.

Conversely, the prevalence of the competitive OH^- ions in the solution beyond the pH_{PZC} of the sorbents resulted in deprotonation of their surfaces and triggered repulsive forces against MO anions, leading to a reduction in MO uptake by both sorbents. So, pH 3.0 was considered for conducting the experiments of the succeeding parameters.

Electrostatic interaction cannot be regarded as the only driving force for MO sorption by MS/Cs/An composite and considerable contributions from other hydrophobic forces (hydrogen bonding) may be counted (Fig. 4.7b), especially at $pH>pH_{PZC}$. Such forces can be correlated to the hydrophobicity of graphite and organic matter constituents of the addressed sorbents. The hydrogen bonding interaction can be categorized into two styles: (1) Yoshida H-bonding and (2) dipole–dipole H-bonding. The former interaction style occurs between the aromatic rings of the MO and the hydroxyl groups upon addressed sorbents surfaces. Whereas, the latter interaction links the nitrogen and oxygen atoms of the MO (H-acceptor) with the accessible hydrogen atoms of the MS/Cs/An hydroxyl and carboxyl groups (H-donor).

Table 4.2 Changes in residual MO concentration, amount of MO sorbed, removal rate (%) as a function of pH [Dose; 35 mg, 25 ml of MO; 50 ppm, pH (2-9), RPM; 200, time; 120 minutes, temp; 20C°]

pH	**Initial MO conc. (C_o ppm)**	**Residual MO conc. (C_e ppm)**	**Removal rate R %**	**MO sorbed (q_e mg g^{-1})**
2	50	1.2	97.6	34.86
3	50	1	98.0	35.00
4	50	1.5	97.0	34.64
5	50	2	96.0	34.29
7	50	2.1	95.8	34.21
9	50	3	94.0	33.57

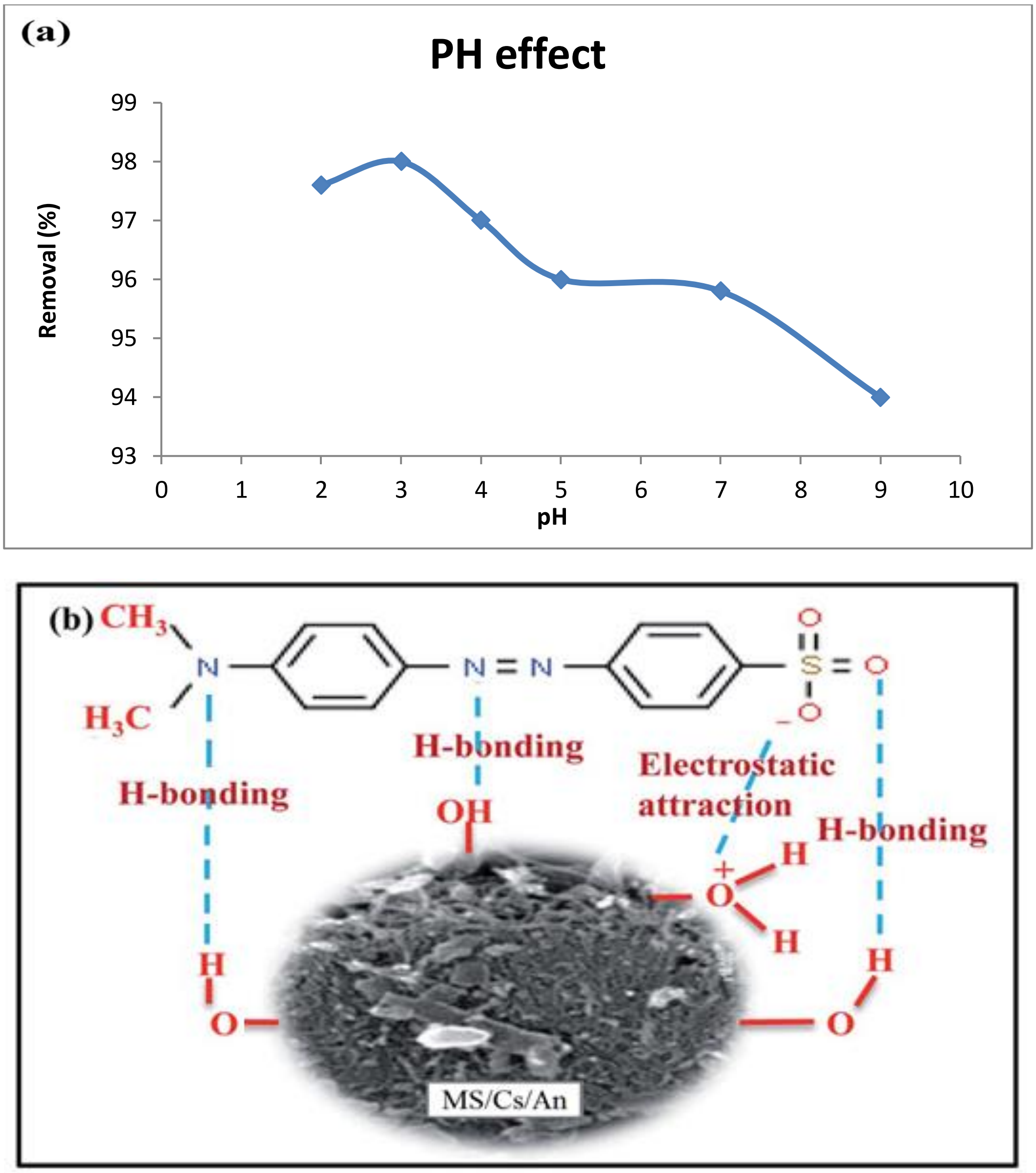


Fig. 4.7 Effect of pH on MO removal by MS/Cs/An composite (a), schematic diagram showing the mechanisms of MO sorption by MS/Cs/An composite (b).

4.2.2 Effect of contact time

The adsorption outline of MO by MS/Cs/An composite at several selected times (5–150 min) is demonstrated in Table 4.3 and Fig. 4.8. The results revealed that adsorption was very rapid at the beginning 5 to 30 min (from 68.8% to 89.6%), this behavior is because of the electrostatic interactions which facilitate the diffusion of extra dye molecules to the interior free sites. Moreover, during the initial stage, a large number of vacant surface localities were available, while at mixing times > 30 min and ≤120 min was (from 89.6%

to 98.4%), this behavior is because of the remaining vacant surface sites after a lapse of time were difficulty packed attributable to the repellence forces amongst the dye molecules on the solid and bulk phases. With increasing contact time beyond 120 min, there is no further perceptible increase in the MO adsorption by the sorbent (R=98.6% at 150 min). The diffusion becomes more difficult as the vacant volume within the adsorbent decreases. Thus, the affinity of sorbent towards MO molecules decreased. This indicates that equilibrium was attained at 120 min; therefore, 120 min was deployed as an equilibrium time for the other experiments

Table 4.3 Changes in residual MO concentration, amount of MO sorbed, removal rate (%) as a function of contact time [Dose; 35 mg, 25 ml of MO; 50 ppm, pH (3), RPM; 200, time; (5-150) minutes, temp; 20C°]

Time (minutes)	**Initial MO conc. (C_o ppm)**	**Residual MO conc. (C_e ppm)**	**Removal rate R %**	**MO sorbed (q_t mg g^{-1})**
5	50	15.6	68.8	24.57
10	50	12.3	75.4	26.93
15	50	8.4	83.2	29.71
30	50	5.2	89.6	32.00
60	50	2.5	95.0	33.93
90	50	2.1	95.8	34.21
120	50	0.8	98.4	35.14
150	50	0.7	98.6	35.21

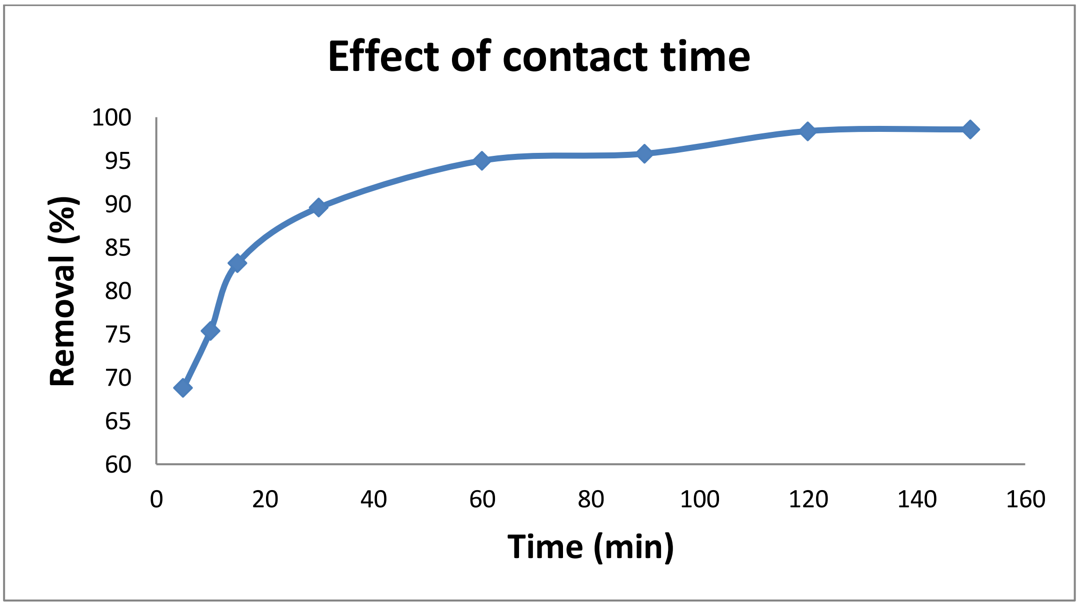


Fig 4.8 Effect of contact time on MO removal by MS/Cs/An composite.

4.2.3 Effect of initial concentration

The adsorption of MO was conducted at different dye concentrations as shown in Fig. 4.9. The results showed that increasing MO concentration from 20 to 80 ppm, cause a decrease in the removal percent R% from 99% to 64.6%. However, the amount of MO sorbed (q_e, mg g^{-1}) increased with raising the initial concentrations. The progressive collision of MO ions with the active sites of the composite with increasing the initial concentration was the key factor in such enhancement. Also, the enhancement of MO sorption was derived by the increase in the mass gradient that acted as a driving force for transferring the MO ions onto the MS/Cs/An composite surface. The overall reduction in R% at high initial concentrations was associated with the deficiency in the vacant sites that could accommodate the MO ions from solution. Unlike removal efficiency and sorption capacity that are controlled by the operating conditions, distribution coefficient K_d can be used as a true metric to merit the adsorbent true performance. K_d is a representative ratio for the analytic concentration among both solid and liquid phases at equilibrium. In the current study, the MO distribution coefficient K_d revealed a marked decrease from 70.7 to 1.3 L g^{-1} with increasing initial MO concentrations from 20 to 80 mg L^{-1} Table 4.4. Therefore, aqueous dye solution with initial MO concentration 50 mg/L was appropriated for all the adsorption studies to verify equilibrium accomplishment.

Table 4.4 Changes in residual MO concentration, amount of MO sorbed, removal rate (%) as a function of initial MO concentrations [Dose; 35 mg, 25 ml of MO; 20-80 ppm, pH (3), RPM; 200, time; 120 minutes, temp.; 20C°]

Initial MO conc. (C_o ppm)	**Residual MO conc. (C_e ppm)**	**MO sorbed (q_e mg g^{-1})**	**Removal rate R %**	**Kd (L g^{-1})**
20	0.2	14.14	99.00	70.71
30	0.4	21.14	98.7	52.86
40	0.6	28.14	98.50	46.90
50	1	35.00	98.00	35.00
60	8.5	36.79	85.8	4.33
70	19.3	36.21	72.4	1.88
80	28.3	36.93	64.6	1.30

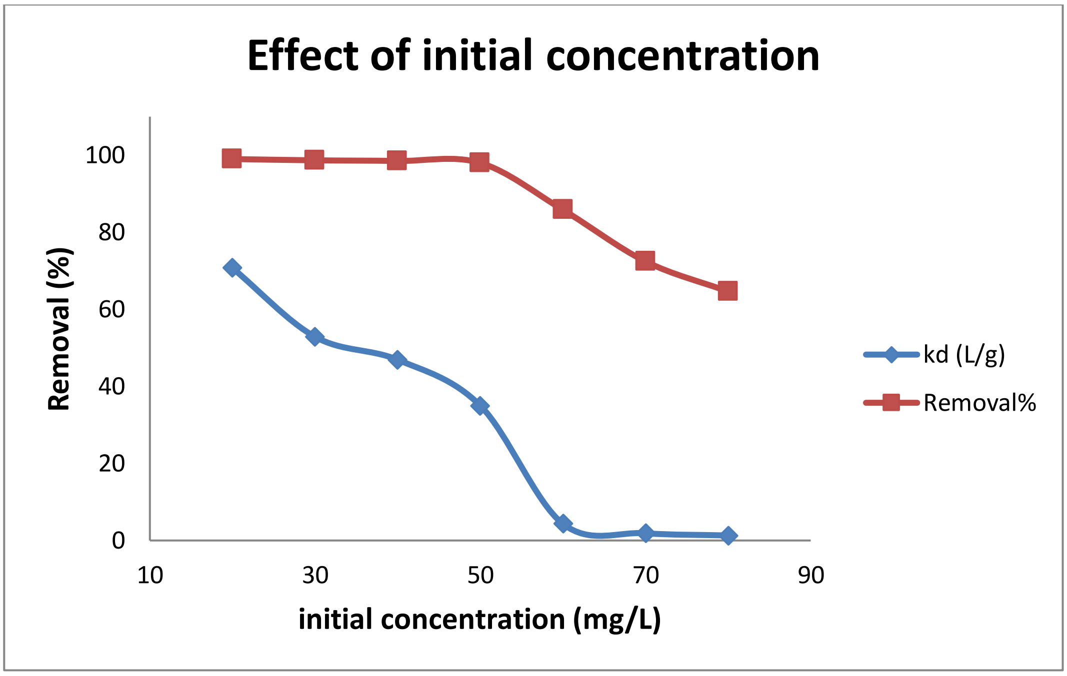


Fig 4.9 Effect of initial concentration on MO removal and Kd by MS/Cs/An composite.

4.2.4 Effect of adsorbent mass

Increasing the composite mass from 5 to 35 g was accompanied by an increase in MO removal from 43.4% to 98% (Table 4.5 & Fig. 4.10). This justifiable increase in MO removal was interrelated to the surface area of the adsorbent and hence the accessible sites for MO sorption. Beyond 35 mg of composite mass, no appreciable increase in MO uptake was observed (≈99.6% for 40 and 50 mg). This indicates that the equilibrium state was achieved.

Therefore the dose (35 mg) was the optimum dose and appropriated for all the adsorption studies to verify equilibrium accomplishment. As the quantity of adsorbent raises, the number of active sides obtainable for adsorption also increases thus the removal percentage also increases. But owing to the overlapping between the active sides themselves, not all the obtainable active sides are available during adsorption thus, the amount adsorbed mg/g of adsorbent may be decreased.

Table 4.5 Changes in residual MO concentration, amount of MO sorbed, removal rate (%) as a function of absorbent mass [Dose; 5-50 mg, 25 ml of MO ;50ppm , pH (3), RPM;200, time ; 120 minutes, temp. ;20C°]

Dose **(mg)**	**Initial MO conc.** **(C_o ppm)**	**Residual MO conc.** **(C_e ppm)**	**Removal rate** **R %**	**MO sorbed** **(q_e mg g^{-1})**
5	50	28.3	43.4	108.50
10	50	25.2	49.6	62.00
20	50	20.8	58.4	36.50
30	50	8.1	83.8	34.92
35	50	1	98	35
40	50	0.2	99.6	31.13
50	50	0.1	99.8	24.95

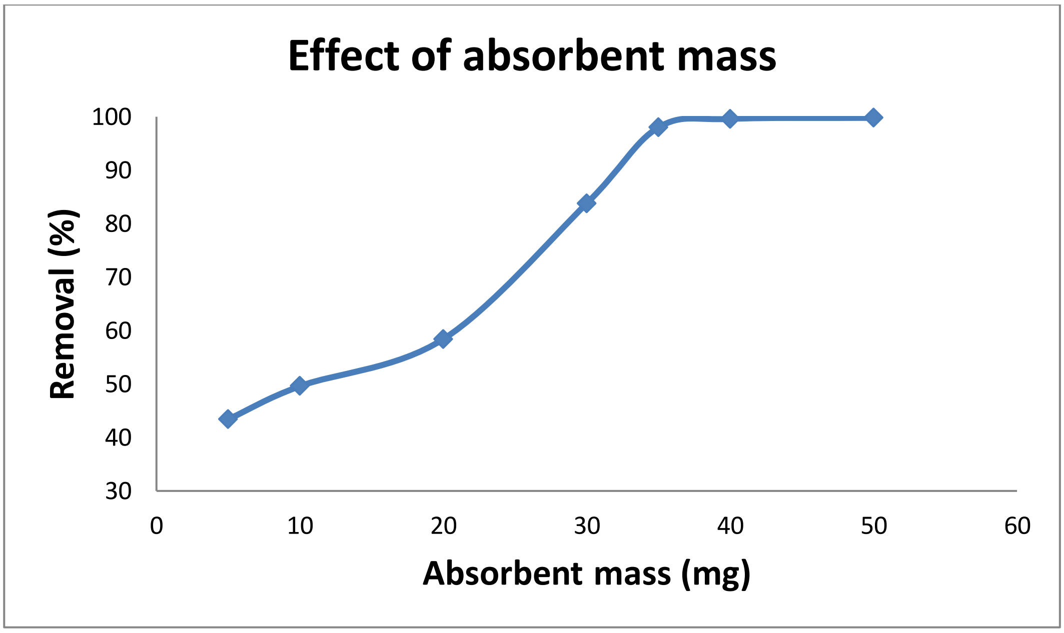


Fig 4.10 Effect of absorbent mass on MO removal by MS/Cs/An composite.

4.2.5 Effect of agitation speed

The sorption of MO under different mixing speeds (50 to 250 rpm) was carefully examined. At the speed from 50–150 rpm, the R% rapidly increased from 84% to 93.6% Table 4.6 & Fig 4.11. The obtained results demonstrate that increasing the shaking rate up to 150 rpm has a positive result on the adsorption of MO onto the MS/Cs/An composite. These results could be ascribed to the enhancement in dye dispersion and increase the exposed adsorbent surface area to the dye molecules. Additionally, raising the agitation rate improves the diffusion of dye towards the adsorbent surface. In contrast, a further rise in the agitation velocity up to 200 rpm creates a decline in the adsorption affinity. This declining could be as a result of a further speedup in the agitation rate beyond 200 rpm could diminish the attraction forces between the adsorbent and MO and promote the occurrence of dye desorption process. Thus agitation speed of 200 rpm selected as the optimum speed and appropriated for all the adsorption studies to verify equilibrium accomplishment.

Table 4.6 Changes in residual MO concentration, amount of MO sorbed, removal rate (%) as a function of agitation speed [Dose; 35 mg, 25 ml of MO; 50 ppm, pH (3), RPM; (50-250), time; 120 minutes, temp; 20C°]

Agitation speed (RPM)	**Initial MO conc. (Co ppm)**	**Residual MO conc. (Ce ppm)**	**Removal rate R %**	**MO sorbed (q_e mg g^{-1})**
50	50	8	84	30.00
100	50	3.8	92.4	33.00
150	50	3.2	93.6	33.43
200	50	1	98	35.00
250	50	1.1	97.8	34.93

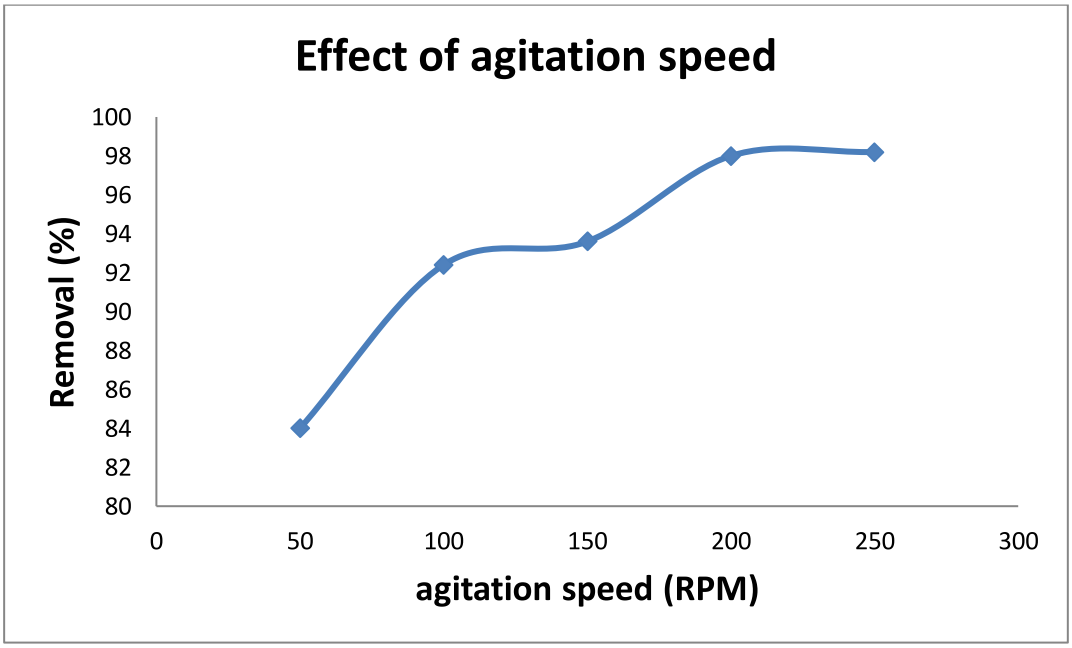


Fig 4.11 Effect of agitation speed on MO removal by MS/Cs/An composite.

4.3 Thermodynamic constants

The temperature has important effects on the adsorption process. The influence of temperature (K^0) on the removal percentage of the M.O by MS/Cs/An composite was plotted at 288, 293, 298, 308, 318, and 328 K^0 as shown in Fig.4.12.a.

The results displayed in Fig. 4.12.b, shown that the uptake capacity raised from 34.6 to 35.4 mg/g with raising the temperature from 288 to 328 K^0. Higher temperature leads to an increase in the kinetic energy of M.O ions and MS/Cs/An particles which, causes an increase in the chances of attraction between adsorbate and adsorbent materials. Hence, the adsorption process of M.O onto MS/Cs/An is endothermic in nature. Also, it is well known that the increase in the adsorbed amount of M.O with increasing the temperature is may be due to the enhancing of the sorptive forces of the MS/Cs/An active sites towards M.O species. Furthermore, increasing the sorptive forces among the contiguous for the adsorption of M.O onto MS/Cs/An as shown in Table 4.7. The negative value of ΔG ranged from -7.55 to -12.14 kJ.mol^{-1} affirm the probability of the operation as a spontaneous adsorption reaction. ΔH and ΔS were found to be 25.54 kJ.mol^{-1} and 115 J.mol^{-1}.K^{-1}, respectively; the positive value of the enthalpy implying that the process is endothermic and low temperature makes the adsorption easier. The enthalpy value 25.54 kJ.mol^{-1} is also confirmed that the adsorption is physicosorption as it is lower than that for chemisorption. Therefore, the adsorption of the MO under examination onto MS/Cs/An is probably due to physicosorption. This conclusion showed the fundamental reaction between the MO and the MS/Cs/An to beat most electrostatic interactions. Besides, the lower positive value of ΔS 115 J.mol^{-1}.K^{-1} suggests random less at the liquid/solid mediator during the MO adsorption onto MS/Cs/An in the aqueous solution.

Table 4.7 Changes in residual MO concentration, amount of MO sorbed, as a function of temperature [Dose; 35 mg, 25 ml of MO; 50 ppm, pH (3), RPM; 200, time; 120 minutes, temp.; 15-55C°]

Temp. (k^0)	**C_e**	**q_e**	**Q_e/C_e**	**$Ln(q_e/C_e)$**	**($1/T\ K^0$)**	**$\Delta G/kJ\cdot mol^{-1}$**	**$\Delta H/kJ\cdot mol^{-1}$**	**$\Delta S/J\cdot mol^{-1}\cdot k^{-1}$**
288	1.5	34.64	23.1	3.140	0.00347	-7.55	25.54	115
293	1.2	34.86	29.05	3.369	0.00341	-8.12		
298	1	35.00	35.00	3.555	0.00336	-8.70		
308	0.8	35.14	43.93	3.783	0.00325	-9.85		
318	0.6	35.29	58.81	4.074	0.00314	-11.00		
328	0.4	35.43	88.57	4.484	0.00305	-12.14		

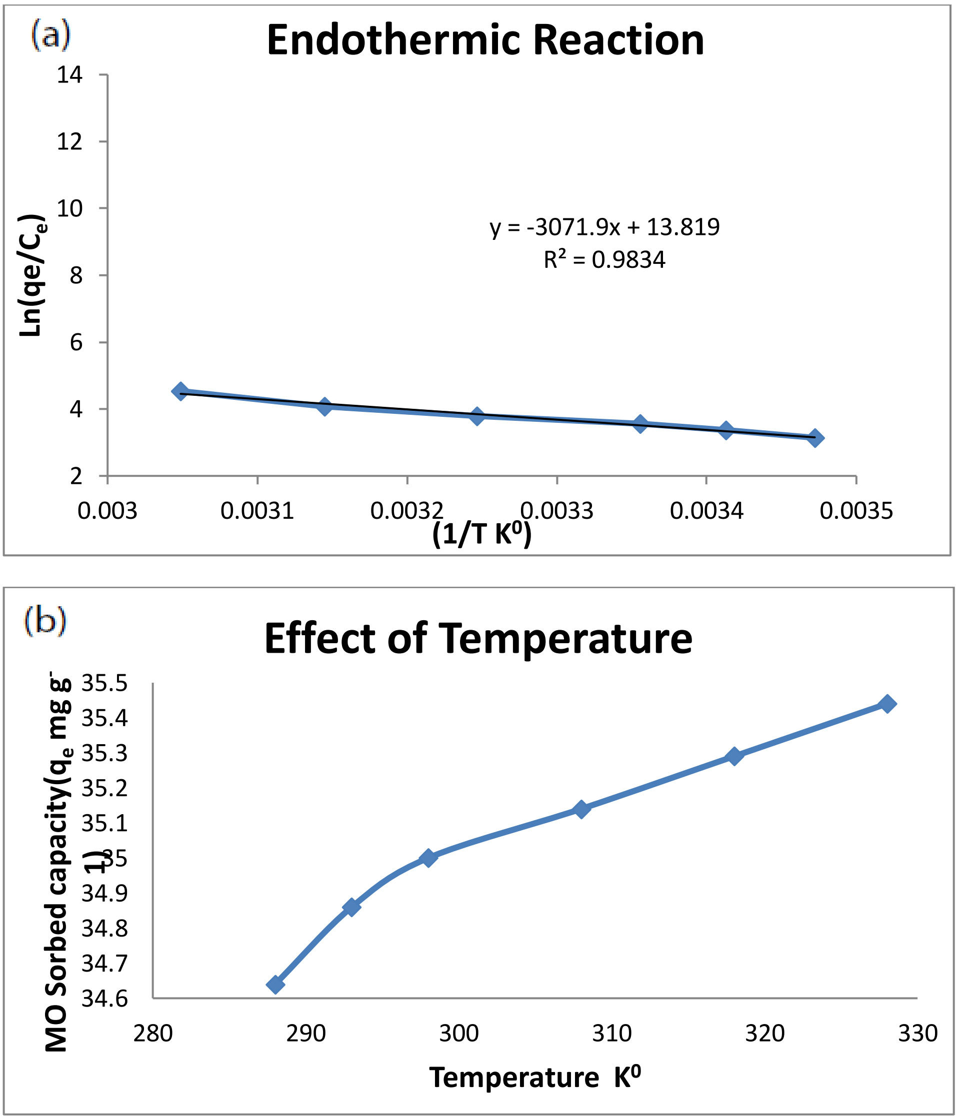


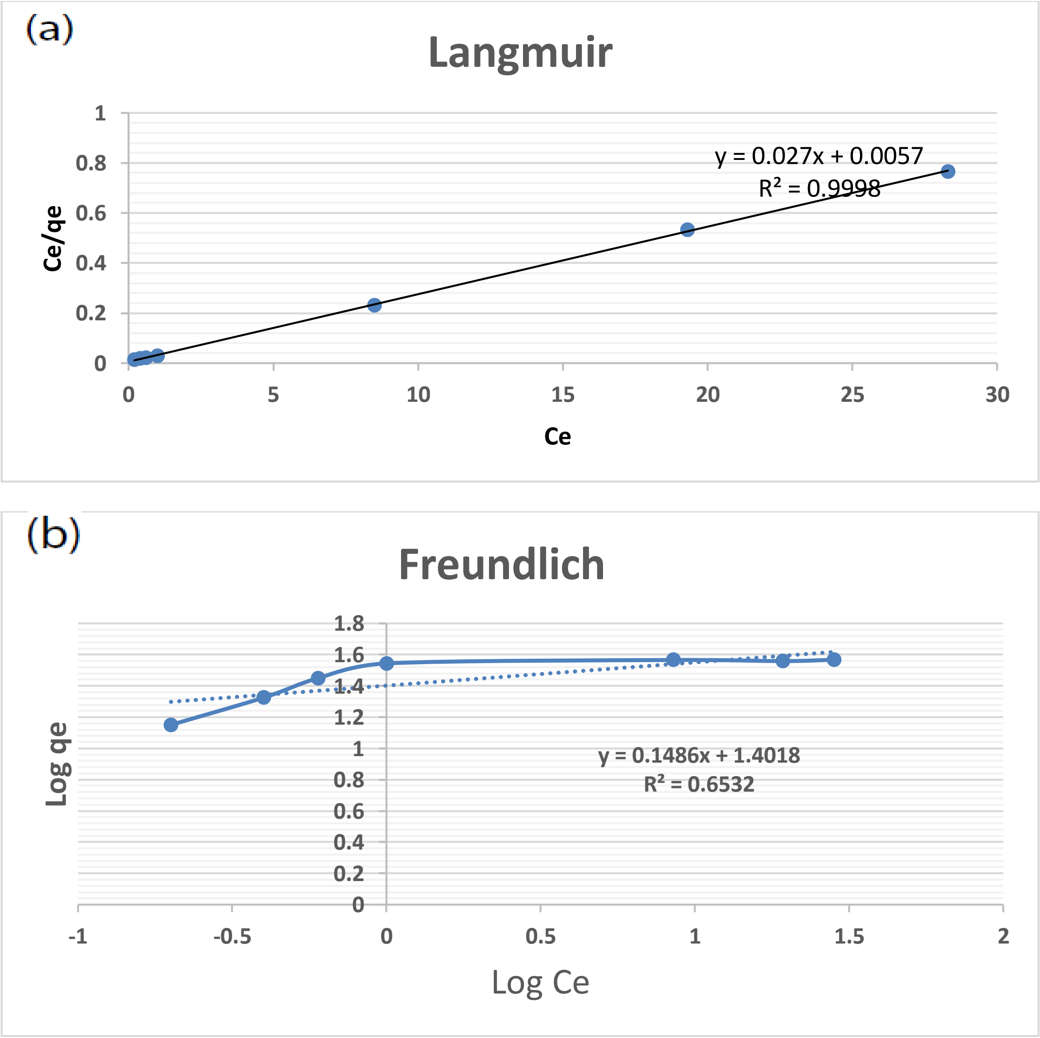
Figure 4.12 Plot of In (q_e/C_e) versus 1/T for the estimation of thermodynamic parameters (a), effect of temperature on MO removal by MS/Cs/An composite (b).

4.4 Adsorption isotherms

The linear equations of the most three customarily applied isotherm models "Langmuir, Freundlich, and Temkin models" were applied in the current study to clarify and interpret the mode of fundamental interaction between M.O ions in the solution and the active sites on the MS/Cs/An composite's surface. The parameters of these linear equations were computed in Table 4.8, and the linear plots of these equations are shown in Figure 4.13a-c. Sorption isotherm techniques are critical helpful tools for understanding the interaction mechanism between M.O and MS/Cs/An composite. In order to investigate the suitable model, the theoretical amounts of M.O sorption (mg/g) were evaluated from the model's equations, equilibrium concentration of the adsorbate ions (mg/L), which can be calculated from the plot between C_e/q_e versus C_e. q_{max} and b are Langmuir constants related to maximum sorption capacity (monolayer capacity) (mg/g) and energy of sorption (L/mg). Likewise, K_F and n are Freundlich constants related to sorption capacity and sorption intensity, respectively, which can be calculated from the plot of log (q_e) versus log (C_e). The value of constant n showed the degree of non-linearity between the solution concentration and adsorption, if n=1 the adsorption is linear, n<1 the adsorption is a chemical process, n>1 the adsorption is a physical process, n value (6.73) greater than 1 and this indicate the adsorption is physical process. The Temkin isotherm has generally been applied. Therefore, plotting q_e versus ln C_e, enables the determination of the constants A and B. While, B=RT/b is the Temkin constant related to the heat of sorption (J/mol), A is the Temkin isotherm constant (L/g), R the gas constant ($8.314\ J.mol^{-1}.K^{-1}$), b is Temkin isotherm constant and T is the absolute temperature (K). In the recent study, Langmuir showed an excellent fitting to the experimental data for the three sorbents with a high correlation coefficient (0.9998), Fig. 4.13a. This assumed that the MO uptake by the studied composite was homogeneous (monolayer) in nature through iso-energetic binding sites on the MS/Cs/An composite's surface. Langmuir constant was 4.737 L/mg. Furthermore, the R_L (Langmuir equilibrium parameter) values (0.0042) that was calculated using “$R_L= 1/(1+bC_0)$” equation, confirmed a favourable sorption of MO ions (favourable, $0<R_L<1$) by the composite and the maximum monolayer adsorption capacity (q_{max}) of M.O via MS/Cs/An composite by Langmuir model was (37.04) mg/g. The heat of adsorption has been studied by Temkin since it provides a good fitting to describe the M.O sorption process in the recent work. Temkin model evaluates a gradual increase in the heat of adsorption for the increase of surface area using MS/Cs/An.

Table 4.8 Isotherm parameters of the MO adsorption by (MS/Cs/An) composite

Langmuir				**Freundlich**			**Temkin**			
q_{max} (mg/g)	**b (L/mg)**	**R^2**	**R_L**	**K_F (mg/g)**	**n**	**R^2**	**B (J/ mol)**	**A (L/g)**	**b**	**R^2**
37.04	4.737	0.99	0.0042	25.22	6.73	0.6532	3.826	1096.6	647.6	0.716



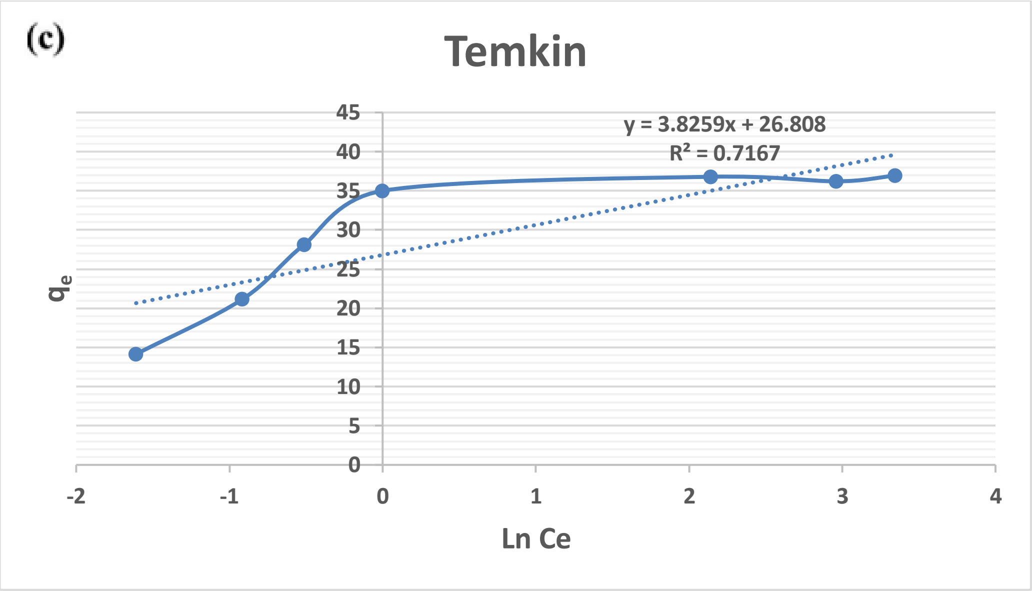


Fig 4.13 Isotherms constants (Langmuir isotherm a, Freundlich isotherm b, Temkin isotherm c) of MO adsorption onto MS/Cs/An composite by linear curves.

4.5 Sorption kinetics

The kinetic data of MO removal by MS/Cs/An composite was studied based on the linear form of the most commonly used models pseudo-1st order "PFO", pseudo-2nd order "PSO", and inter-particle diffusion models. The equations that express the linear formula of these models and the values of their related constants were compiled in Tables 4.9.

The fitted results using the PSO equation is better than that using the PFO one (Fig. 4.14a, and b), as expressed by the high determination coefficient (R^2=0.9999) of the PSO equation compared to that PFO with an experimental (qe^{exp}) and theoretical (qe^{cal}) values of 35.14 and 35.84 mg g^{-1}, respectively. The PSO rate constant is 0.0087 g mg^{-1} min^{-1}.

On the other hand, the graphical presentation of the intra-particle diffusion model (qt vs. $t^{0.5}$) for MO sorption by MS/Cs/An composite yielded a multi-linear plot deviating out of the origin Fig. 14c. This behavior affirmed that intra-particle diffusion was not the only rate-principal step in MO adsorption process.

The sorption of Methyl orange from aqueous media by the synthesized MS/Cs/An composite can be described by three consecutive steps: (i) the transport of sorbate from the bulk solution to the outer surface of the sorbent by molecular diffusion, known as external diffusion, (ii) internal diffusion that is, the transport of sorbate from the particle surface into interior sites, and (iii) the sorption of the solute particles from the active sites into the interior surfaces of the pores. The overall rate of the sorption process will be controlled by the slowest step; that is, the rate-limiting step. The nature of the rate-limiting step in the batch system can be determined from the properties of the solute and sorbent. Rates of sorption are usually measured by determining the change in the concentration of sorbate with sorbent as a function of time.

The sorption rates for the intra-particle diffusion, K_p were calculated from the slopes of the linear portions of the respective plots with units of mg/g/min$^{0.5}$ (not the true reaction rate, but relative rates which are useful for comparative purposes). The two plots have the same general features, initial curved portion followed by linear portion and plateau. The initial curve portions are attributed to the boundary layer diffusion effects. While the linear portions are a result of the intra-particle diffusion effects and the plateau is attributed to the equilibrium. An extrapolation of the linear portion of the plots back to the time$^{0.5}$ axis provides intercepts that are proportional to the extent of boundary layer thickness. The larger the intercept, the greater is the boundary layer effect.

Table 4.9 Adsorption kinetic parameters for MO removal using (MS/Cs/An) composite

Pseudo- 1st rate			**Pseudo- 2nd rate**			**Diffusion rate**		
K_1 (min^{-1})	**qe^{cal} ($mg\ g^{-1}$)**	**R^2**	**K_2 (min^{-1})**	**qe^{cal} ($mg\ g^{-1}$)**	**R^2**	**K_p ($mg\ g^{-1}\ min^{-0.5}$)**	**C ($mg\ g^{-1}$)**	**R^2**
0.0211	12.58	0.93	0.0087	35.84	0.99	0.9842	24.67	0.855

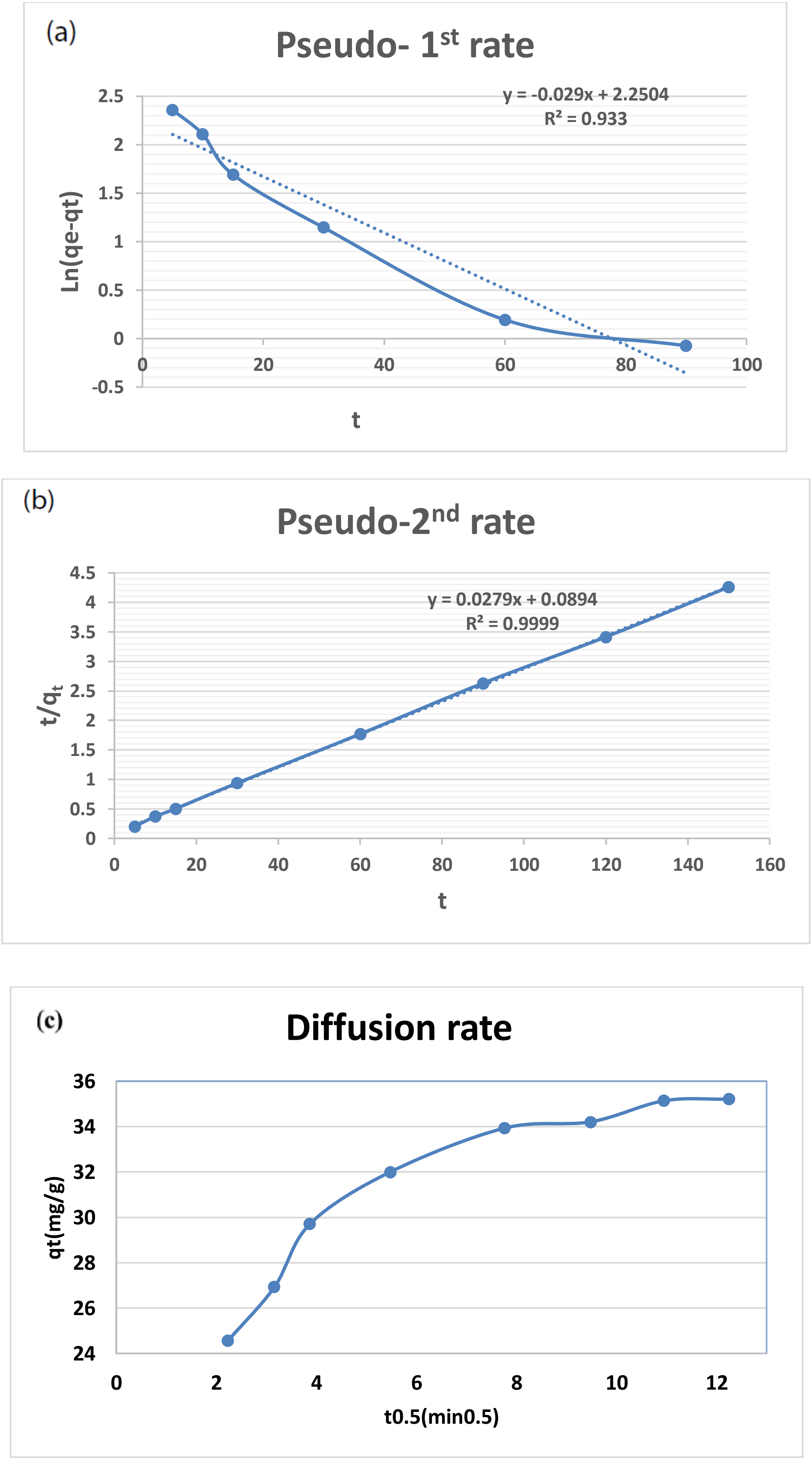


Fig. 4.14 Plot of pseudo first-order kinetic model (a), pseudo second-order kinetic model (b), intra-particle diffusion model (c) for MO uptake by MS/Cs/An composite

Chapter Five

Conclusions and Recommendations

5.1 Conclusions

Within the outcomes of the present study, the following conclusions are derived: (MS/Cs/An) composite is represented as an efficient adsorbent material for the removal of Methyl orange from aqueous solution. Several parameters (time, agitation speed, adsorbent mass, pH, and initial dye concentration) were examined. The isotherms, kinetics and thermodynamics of adsorption were also studied.

The results demonstrated that the optimum conditions are (time 120 min, agitation speed 200 rpm, adsorbent mass 35 mg; pH 3, and initial MO concentration is 50 mg/L. Adsorption isotherms indicate that the maximum monolayer coverage is 37.04 mg/g. The adsorption isotherm data fitted well to the Langmuir isotherm (R^2=0.9998) while the experimental data fitted very well to the pseudo-second-order kinetic model (R^2=0.9999). This study suggests that (MS/Cs/An) composite adsorbent can be used effectively for the adsorption of MO from aqueous solution. Thermodynamic parameters for the adsorption shown that the negative value of ΔG ranged from –7.55 to –12.14 kJ.mol^{-1} confirm the feasibility of the process and spontaneous nature of adsorption. The values of ΔH and ΔS are found to be 25.54 kJ.mol^{-1} and 115 J.mol^{-1}.K^{-1}, respectively and the adsorption is an endothermic reaction, the enthalpy value 25.54 kJ.mol^{-1} is also confirmed that the adsorption is physicosorption as it is lower than that for chemisorption

Through the current study, the following deductions could be formulated:

- The MO isotherm and kinetic data were described well by the Langmuir and PSO models, respectively.
- The homogenous MO sorption by the (MS/Cs/An) composite was a pH-dependent process and the maximum monolayer coverage (qmax=35 mg g^{-1}) was attained at pH 3.0 and ambient temperature.

- The multi-linearity of intra-particle diffusion fitting unquestionably affirmed that the external (film) ($0<T\leq15$ min) and intra-particle diffusions ($15<T\leq60$ min) were the main driving steps for MO sorption by (MS/Cs/An) composite.
- Electrostatic interaction was the principal driving mechanism for MO sorption by (MS/Cs/An) at pH < pHPZC, via the protonation process of its oxygen-holding groups. While Yoshida and dipole–dipole H bonding mechanisms can explain the MO sorption by the addressed composite, especially at pH > pHPZC.
- Finally, the (MS/Cs/An) composite is an eco-friendly, reliable and affordable sorbent for the remediation of MO contaminated water.

5.2 Some recommendations and future prospects:

- Using this composite in the process of adsorbing other dyes and ions.
- Improving the properties of seaweed composite by studying the change of its physicochemical properties by activating it using chemicals, which increases its specific surface and thus increases the adsorption yield.
- Attempting to stimulate this composite using other inorganic solutions (phosphoric acid, nitric) or organic (acids, sterone, oxalic and lactic).
- Exploitation of this composite in the treatment of heavy metal salts from their aqueous solutions and organic colorants Or some basic materials for pesticides, while studying the properties of the thermodynamic adsorption process and kinetics.
- Study other types of seaweed that have the ability to remove organic and inorganic pollutants from water sewage.
- Study the efficiency of pollutant removal using seaweed composite for urban wastewater, industrial and hospital for example.

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دولة ليبيا

وزارة التعليم والبحث العلمي

الجامعة الأسمرية الإسلامية
كلية العلوم-قسم الكيمياء

مقترح مقدم لإستكمال درجة الإجازة العليا (ماجستير) في الكيمياء بعنوان:

دراسة كفاءة الإمتزاز في إزالة بعض أصباغ الأزو بإستخدام الفحم المنشط الناتج من المخلفات الزراعية

Study Of Adsorption Efficiency To Remove Some Of Azo Dyes Using Activated Carbon Derived From Agr-Residues.

إعداد الطالب:

أيوب مفتاح الفلوس

تحت إشراف:
د. خالد أحمد الفلوس
مشرف مشارك:
د. مختار المبروك أبورزيزة
د. فتحي محمد أحمد

العام الجامعي (2022)

الملخص

العديد من مناطق العالم المختلفة تواجه مشكلة تلوث المياه السطحية والجوفية بالأصباغ. حيث تعتبر صناعة الأصباغ والطباعة المصدر الرئيسي لتلوث المياه، ويعتبر الإستخدام المفرط للأصباغ هو السبب الرئيسي لهذا التلوث.

يهدف هذا البحث إلى إيجاد عملية بسيطة واقتصادية لتقليل تركيزات صبغة الميثيل البرتقالي في المحاليل المائية ذات القدرة العالية على الإمتصاص. ولتحقيق هذا الهدف أجريت العديد من التجارب المخبرية على امتزاز الميثيل البرتقالي باستخدام الكربون المنشط. في بحثنا هذا حاولنا القيام باستخدام طريقة لتقليل تكلفة إنتاج الكربون النشط عن طريق تحضير مركب (الأعشاب البحرية المعدلة / محلول الكيتوزان / الأنثراسين). ثَم خلط الأعشاب البحرية المعدلة (MS) كمادة ابتدائية، بشكل متجانس مع الأنثراسين (An) (نسبة 1/4 صلب/صلب) ثُم تذويب المخلوط في محلول الكيتوزان (Cs)، ثَم اختيار هذه الكمية الدقيقة من (An) لتحقيق الهدف المخطط له بأقل التكاليف. ثُم طحن الخليط المتكلس برفق تحت إسم مركب (MS/Cs/An) لاستخدامه لاحقا. ثَم تشخيص الخصائص الفيزيائية والكيميائية للأعشاب البحرية المعدلة (MS) ومركب (MS/Cs/An) من خلال التحليل الطيفي للأشعة تحت الحمراء FT-IR، وحيود الأشعة السينية XRD، والتحليل الحراري الوزني (TGA, DSC)، كذلك ثَم فحص وتشخيص شكل ومساحة السطح, باستخدام الفحص المجهري الإلكتروني (SEM) ونظرية (BET) على التوالي.

ثَم فحص الخصائص الإمتزازية لمركب (MS/Cs/An) من حيث جرعة المادة المازة، ودرجة الحموضة، ودرجة الحرارة، ووقت التلامس، وسرعة التحريض. أجريت الإختبارات التجريبية على دفعات.

ثَم تفسير بيانات الإتزان بإستخدام أيزوثرمات الإمتزاز وهي نماذج لانجمير وفرندليش وتمكين, حيث وجد أن الإمتزاز يتبع أيزوثرم لانجمير. يشير معامل الفصل R_L, إلى أن إمتزاز الميثيل البرتقالي على المادة الممتزة كان ملائماً, وأن أقصى سعة إمتزاز أحادية الطبقة (q_{max}) كانت (37.04) مجم/جم. إنخفض معامل توزيع الميثيل البرتقالي K_d من 70.7 إلى 1.3 لتر.جم$^{-1}$ مع زيادة تركيزات الميثيل البرتقالي من 20 إلى 80 مجم.لتر$^{-1}$.

من أجل التحقق من آليات الإمتزاز، ثَم تطبيق ثلاثة نماذج حركية مبسطة، وهي رتبة الدرجة الأولى الكاذبة والثانية الكاذبة ونموذج إنتشار الدقائق داخل الجسيمات لتناسب البيانات الحركية التي ثَم الحصول عليها باستخدام البيانات التجريبية لتركيزات أولية مختلفة. تم تحديد ثوابت معدل سرعة التفاعل للنماذج الثلاثة وتم حساب معاملات الإرتباط. تدعم البيانات الحركية نموذج الرتبة الثانية الكاذبة حيث وجد أن معامل الإرتباط R^2 =0.9999, كذلك كان الإنتشار (الفيلم) الخارجي متبوعًا بالانتشار داخل الجسيمات هو عملية القيادة الرئيسية خلال المرحلة المبكرة من إمتزاز الميثيل البرتقالي.

ثَم حساب العديد من المعاملات الديناميكية الحرارية لعملية الإمتزاز مثل الطاقة الحرة القياسية (ΔG^0)، المحتوى الحراري القياسي (ΔH^0)، والتغير في الإنتروبي القياسي (ΔS^0)، والذي يشير إلى أن النظام الحالي كان تلقائيًا، وعملية الإمتزاز هي عملية ماصة للحرارة في الطبيعة ، والإمتزاز هو إمتزاز فيزيائي.

كان التجاذب الكهروستاتيكي بين المجموعات الوظيفية الحاملة للأكسجين والنيتروجين على سطح MS/Cs/An وأيونات MO هو آلية التحكم الرئيسية في عملية إمتصاص الميثيل البرتقالي، خاصة عند درجة الحموضة $pH < pH_{PZC}$ للمركب. وفي الوقت نفسه، عملية إمتصاص الميثيل البرتقالي بواسطة المركب المعالج يمكن تفسيرها بالمساهمات القيمة من آليات الترابط Yoshida و dipole–dipole H ، خاصة عند درجة الحموضة $pH > pH_{PZC}$.

لذلك، يعتبر المركب المطور كأفضل المواد الممتزة لمعالجة مياه الصرف الصناعي في ليبيا بتكلفة منخفضة وكفاءة ممتازة.