American Journal of Biodiversity
https://biojournals.us/index.php/AJB
ISSN: 2997-3600

A Study on The Removal of Some Environmentally Polluting Textile Dyes Using Thiazole Complexes

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Received: 2024 01, October
Accepted: 2024 15, October
Published: 2024 31, October

Annotation: Study of textile dyes which are chemical substances and compounds used for the purpose of producing and preparing materials that last for a long period. We have previously indicated that in order for a substance to act as a dye, it must be able to fix itself and have the ability to fix on the fabric. There are no chromogens that act as dyes because the presence of a salt-forming group is necessary. Auxochromes and similar groups, regardless of their specialization (as auxochromes) in order to make the color deep, their presence is necessary to make the chromogen a dye. Thus, auxochromes perform two functions.

Keywords: dye, chemical, auxochrome, chromogen, natural dye, mediterranean

INTRODUCTION

Textile dyes:

Dye is a chemical substance and compound that is used to produce and prepare materials that last for a long time on the surfaces of materials. Man has known dyeing for more than 5,000 years, as ancient man benefited from the dyeing process in coloring animal skin, or various materials that he used for important purposes in his life, the most important of which is clothing or clothing, as he colored these clothes for the first time by rubbing them with fruits and plants with beautiful colors, and from here the dyeing process began to grow and spread, and man also worked to benefit from the dyes found in some plants, the most famous of which are: pomegranate, onion, and cumulus, and after expanding this process, man began to use chemical materials to fix this dye for longer periods, and he also developed other types of these dyes, examples of which include the production of picric acid, which worked to provide a yellow dye for clothes, and another scientist named "William Perkin" also discovered another dye with a light purple color, and Germany is considered one of the most important countries in the world Which contributed significantly to the production of various types of dyes.

Types of dyes:

There are four main types of dyes, which are:

1- Natural dyes:

This type of dye can be extracted from some types of plants, especially from fruits, flowers and leaves of plants. Examples of these dyes include: saffron dye, which is extracted from the saffron plant and gives this dye a yellow color. This dye was used specifically in dyeing silk. There is also another dye known as indigo dye, which is extracted from the indigo tree, which is found in large quantities in India. This dye is characterized by giving it a dark blue color, and it is often used in dyeing wool and cotton. As for the burdock dye, it gives both black and brown colors, and is used in dyeing cotton and silk. There is also a famous type of dye that is still used to this day, which is henna dye. This dye is characterized by giving it a natural orange color, and it is often used in dyeing hair, especially for women. As for animal dyes, the most important and famous of them are: red crimson dye, which is produced through Turtle, while the other type is known as Tyrian purple, and this dye is extracted from Mediterranean oysters in particular, and there is also the dye that is extracted from the cochineal worm, which gives a red dye.

2-Synthetic dyes:

Which may include one of these types of dyes, namely: nitrogen dyes, acid dyes, basic dyes, or pre-mineralized dyes.

3-Synthetic dyes:

The beginnings of these dyes were through the discovery of a dye known as mauve, and the manufacture of this dye led to a major scientific revolution in various countries of the world, and coal tar is considered one of the most important raw materials used to manufacture synthetic dyes.

4-Mineral dyes:

Man discovered this type of dyes through a simple method, which is placing clothes in springs of water, which led to a change in the color of the clothes, and the reason for this is that the water contains iron compounds whose interaction with the clothes led to the creation of different colors and dyes.

METHODS

Classification of dyes

Dyes are classified according to their composition and chemical structure, or according to their use on fabric. The first classification is of theoretical value to the chemist but of less importance to the dyer, who is primarily interested in the interaction of the dye with the fabric, textile, or fiber to be dyed.

Chemical Classification:

The chemical composition and structure of dyes is so diverse that it is difficult to classify them into distinct groups, but the following classification is used in this book, in some cases a dye may be placed in one group or another.

1-Nitro dyes. 2- Nitroso dyes. 3- Alzo dyes. 4- Diphenylmethane dyes. 5- Triphenylmethane dyes. 6- Xanthe0 dyes

7- Diphenylamine dyes. 8- Homocyclic dyes. 9- Basin dyes. 10- Intraquinoid dyes. 11- Sulphur dyes. 12- Phthalocyanine dyes.

RESULTS

Classification of dyes according to application:

1-Acid dyes: Dyes Acid

They are sodium salts, sulfonic acids, and nitrophenols. These dyes directly dye animal tissues and fabrics, but not plant ones, so they are widely used on silk and wool.

2-Basic Dyes: Dyes Basic

They are salts of the bases (bases) colored with hydrochloric acid or zinc chloride. This dye is used directly on animal tissues as well as plant tissues that have been fixed by tannic acid. It is often used on cotton and silk.: substantive dyes

3-Direct Dyes

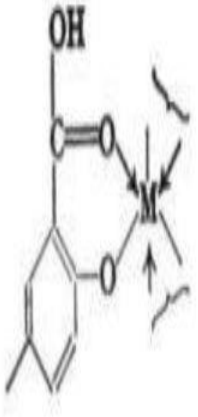
The direct dye that does not require a fixative (it dyes the tissues) animal and plant fibers directly.

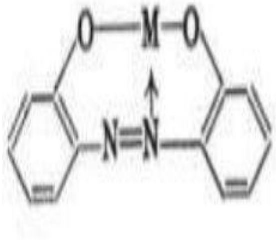
4-Mordant Dyes

They do not dye plant and animal fibers directly, but they require a fixative. If the dye is acidic, the fixative must be basic, and if the dye is basic, the fixative must be acidic. For acidic dyes, the fixatives are metallic hydroxide, and for basic dyes, the fixative usually used is tannic acid. Tannic acid: A mixture of organic tanning materials found in oak leaves, tea, etc. It is a light-yellow crystalline powder that dissolves in water Glycerin is used in leather tanning, as a colour fixative during dyeing and as an antiseptic in medicine. For metal fixation the fabric is dipped and immersed in a solution of a metal salt. The fibre (filler) (applied) is then immersed in a solution of the dye, this gives an insoluble coloured fixed dye which is stable when washed. For the second fixation the fabric is immersed in a tannin bath, but since the fixed dye is dark and tends to be unstable dyes, this results in insoluble and lustrous fixed dyes. The colour of the fixed dye depends on the metal used and the most common metals used are chromium, aluminium, iron and tin. Dye fixatives are believed to be internally complex compounds (chelate compounds) formed between the metal and the dye. Most fixed dyes owe their specific properties to the presence of a hydroxyl group. It appears that a dye containing one hydroxyl group will be fixed if this hydroxyl group is an ortho-to-carboxyl, nitroso, azo, or imino group. For example: Chromium, aluminum, and iron usually form internal complexes (chelate compounds) containing three dye molecules, and it is important to note that a sulfonic acid group cannot form a fixed dye.

5-Vat deys

These dyes are insoluble in water, but are reduced by the alkali sodium hyposulfite (dithionate) to alkali-soluble compounds which are easily oxidized again to dye. These reduced compounds are sometimes white or colorless and are therefore called leuco compounds. They directly dye both animal and plant tissues. Vat deys are often used on cotton fabrics.





6-Inherent dyes (developing)

Their color appears in the fabric and they are divided into three groups:

1-ice-color:

Usually used on cotton fabrics by immersing the fabric in the secondary component (phenol or amine) of azo dyes and the dye is developed by immersion in a solution of salt “diazonium”. The name clours-ice was given because the diazonization and coupling are done at low temperatures.

2-Direct cotton dye containing a free amino group is used on the fabric and is subjected to a diazonization process by immersing it in a solution of nitrous acid, followed by immersion in a solution of a secondary component (phenol or amine). Azo dye is then produced and presented.

3-Aniline-Black

It is produced by oxidation of hydrochloroaniline, either by oxidizing the fabric impregnated with the amine salt, or by heating the fabric with a solution of hydrochloroaniline containing an oxidizing agent (potassium chlorate and vanadium salts as a medium).

7-Sulphur Dyes

It is a dye containing sulfur and is soluble in aqueous sodium sulfur, and is used comprehensively and widely for plant tissues, and the dye is generated in the fabric by oxidation in the atmosphere or by oxidation with dilute aqueous potassium dichromate.

8-Rayon Dyes

Viscose rayon and ammoniacal copper oxide silk can be dyed in the usual way while acetate rayon requires special dyes and techniques as well.

9-Organic Dyes

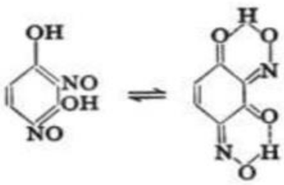
These dyes are not dyes in the sense that they dye tissues but rather materials that are usually insoluble in water and are used to color paints and varnishes. Some dyes have been prepared to be soluble in water and then used as dyes such as phthalo cyanine dyes

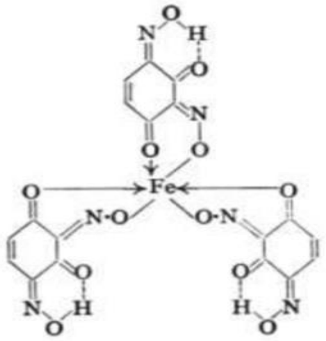
Nitro Dyes:

These dyes contain a nitro group as a chromophore and a hydroxyl group usually as an auxochrome. The simplest nitro dye is picric acid, which was first prepared by Woulfe in 1771, who noted its ability and power to dye silk bright yellow, but the color was not stable. Picric acid is actually the first synthetic dye, and Perkin was the first to find and establish the manufacture of synthetic coal tar dye.

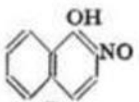
Nitroso Dyes:

In these dyes, the chromophore is a nitroso group and the auxochrome is a hydroxyl group. Nitroso dyes are prepared by the action of nitrous acid on phenols, naphthalates and para-nitroso compounds only. They are useful and beneficial and are often used in the form of iron green fixing dyes in dyeing and printing such as (Fast Green O Fitz 1100) which is prepared by the action of nitrous acid on rosoorcinol and the oxime dye is what gives and provides the fixing dyes. The oxime dye fixes and stabilizes by hydrogen bonding between the molecules).





There are also two nitroso dyes, Gambine R (2-nitroso-1-naphthol, II).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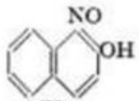

(II)

Azo dyes

The chromophore in azo dyes is the azo group, and the well-known and common exochromes are 2 NH, OH, and 2 NR.

Azo dyes from a practical point of view are classified as basic, acidic, direct, anchoring, and anchoring dyes. The structure and composition of azo dyes is obtained by reduction with stannous chloride and hydrochloric acid, or with sodium hyposulfite (dithionite), where the azo group is cleaved to form primary amines, which are defined and identified

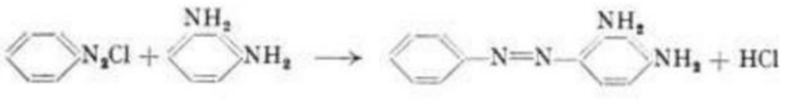
$$Ar{\cdot}N{=}N{\cdot}Ar' \xrightarrow{[H]} Ar{\cdot}NH_2 + Ar'{\cdot}NH_2$$

later:

First - Basic Azo Dyes: These dyes contain 2 NH or 2 NR as auxochrome. (Aniline Yellow) Aminoazobenzene (Yellow Butter)

Dimethylaminoazobenzene)The simplest of the basic azo dyes, but of little value as a dye because they are susceptible to acids.

Phenylene Brown or Bismarck Brown G (Martius 1183) was the first commercial azo dye and was prepared by the action of nitrous acid on an excess of m-phenylene diamine and consists of a mixture of the hydrochlorides of the mono- and bisazo derivatives. Chrysoidine G (110, Witt and Caro 1100) is prepared by the diazation of aniline with m-phenylene diamine, an orange dye and is still used for dyeing cotton on tannin.

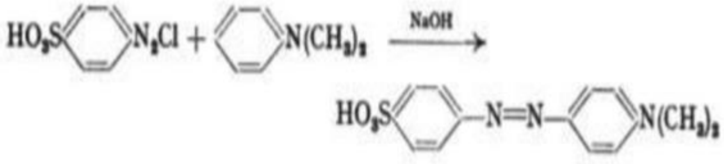


Second - Azo Acid Dyes

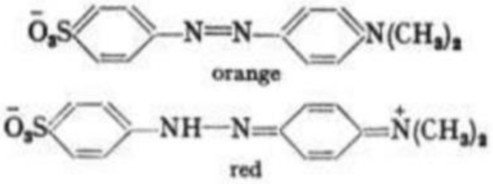
These dyes contain a sulfonic acid group.

The most famous types are:

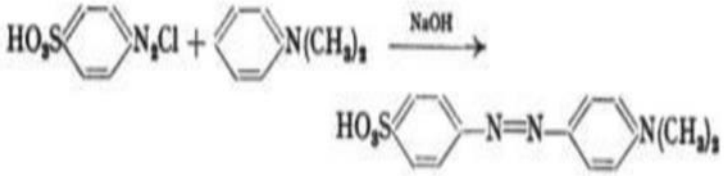
Orange Methyl (litmus dye), prepared by diazation of sulfanilic acid with dimethyl aniline:



It is dyed in unstable color gradations and is used as an indicator or guide, as it is orange in color in an alkaline solution and red in color in an acidic solution:



Dialysis of sulfanilic acid with 1-naphthol gives Orange I (Griess 1108) and with 2-naphthol gives Orange II (Roussin 118). These orange dyes were the first acidic azo dyes on the market.

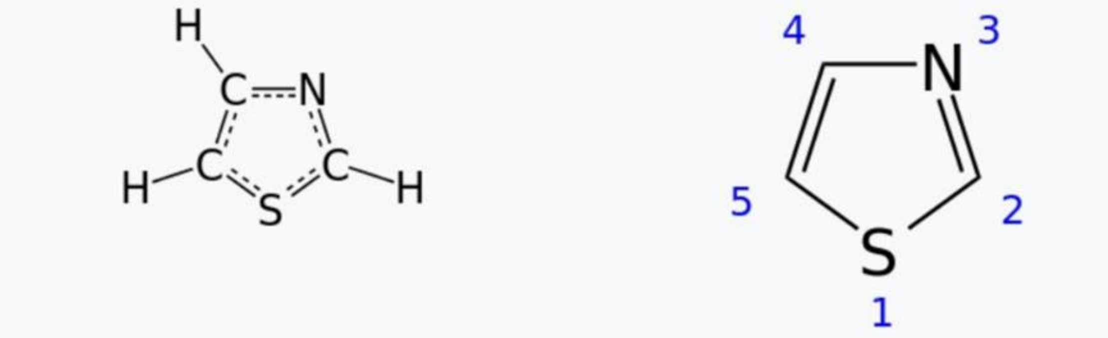


Thiazole

A heterocyclic compound containing both sulfur and nitrogen. Thiazole itself is a pale-yellow liquid with a pyridine-like odor and molecular formula. The term thiazole also refers to a wide family of derivatives. It is noted that the thiazole ring is a component of vitamin thiamine (B1).

Properties of Thiazole

It is a colorless, pale-yellow liquid with an unpleasant odor. Slightly soluble in water. Inhalation or contact with the substance may irritate or burn the skin and eyes. On combustion may produce irritating, corrosive and/or toxic gases. May cause dizziness or vapors may cause suffocation.



Organic Synthesis:

There are several laboratory methods for the organic synthesis of thiazoles. Many thiazole compounds have been prepared

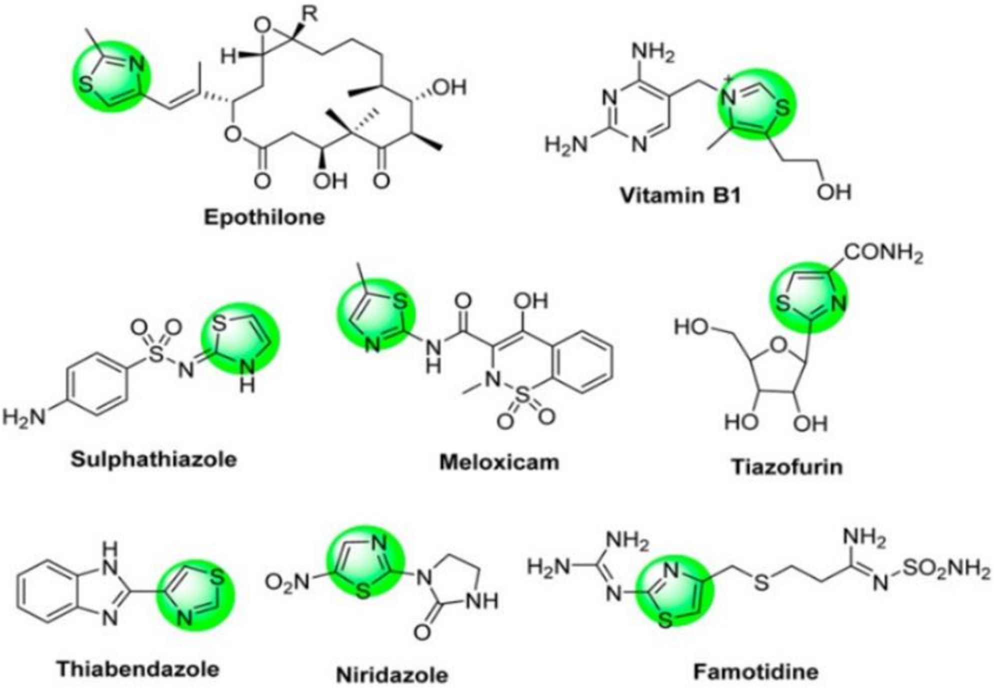


CHART 1. Some thiazole-based synthetic commercial drugs in the market.

Hydrogels: are three-dimensional (3D) interconnected hydrophilic polymer networks, manufactured from natural or synthetic materials, produced by the reaction of one or more monomers, which have the ability to absorb and retain a large amount of water or biological fluids without dissolving in them. Their ability to absorb water is due to the presence of hydrophilic functional groups such as (SO3H, COOH, CONH2, CONH, and OH), and their insolubility results from the chemical or physical entanglement of the polymer chains with each other, which prevents dissolution and maintains the three-dimensional network in the swelling state, as in Figure.(1-9)

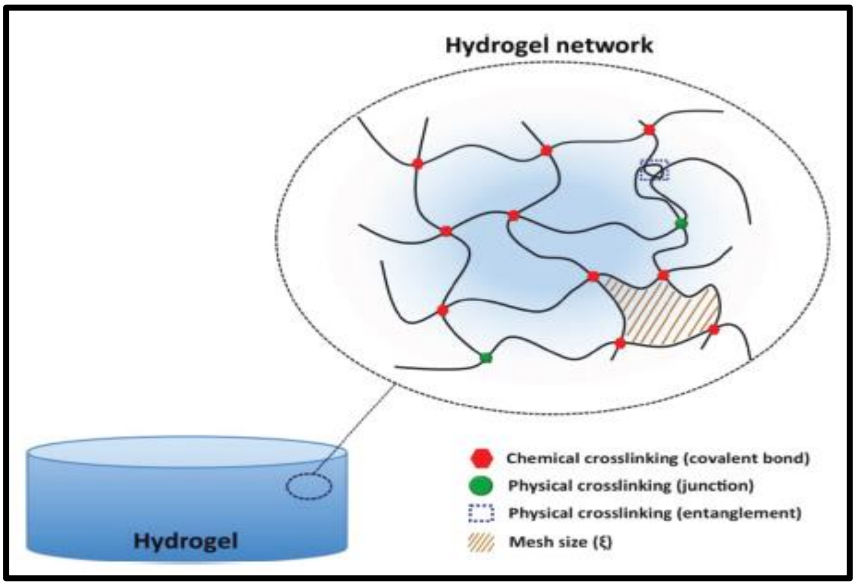


Figure (9-1) Types of entanglement in the hydrogel network [38].

Hydrogels respond to fluctuations in environmental stimuli as they swell and shrink in response to stimuli: physical such as (temperature, electric or magnetic field, light, pressure, and sound), chemical such as (pH, ionic intensity, and solvent composition), and biochemical such as (enzymes and antibody generators), as in Figure.(1-10)

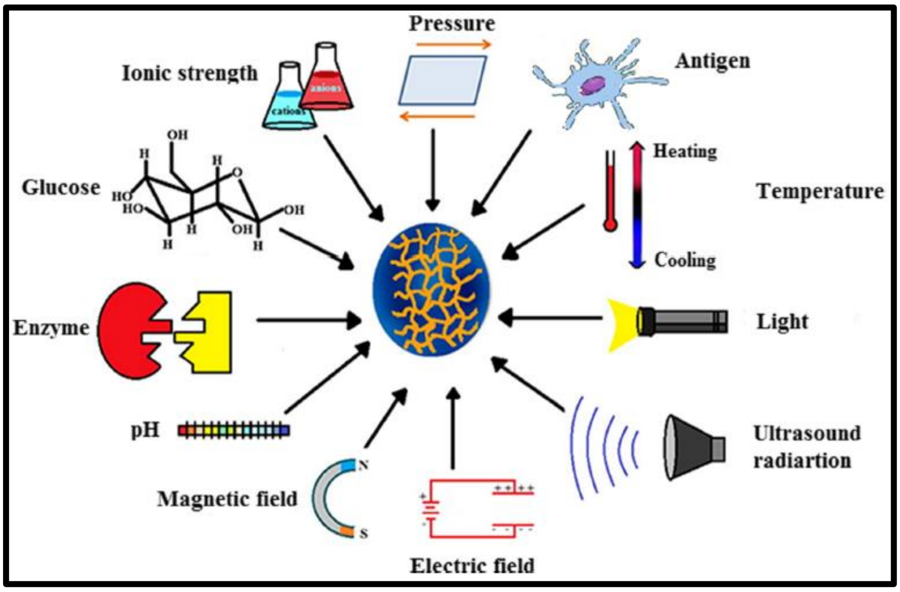


Figure (10-1) Swelling of hydrogels in response to different stimuli [39].

Classification of hydrogels:

Hydrogels are classified according to multiple bases. According to the source, they are classified into (natural, synthetic, and hybrid), and according to the chain structure, they are classified into (homogeneous, which consists of one type of monomers, and common, which consists of different monomers, and multiple interlocking, which consists of two synthetic or natural polymers, one of which is cross-linked and the other is not), and depending on the charge, they are classified into (charged, uncharged, and amphoteric), and according to the type of cross-linking, they are classified into (physical gels, which are cross-linked by physical forces such as hydrogen bonds, and chemical gels, which are cross-linked by chemical forces such as covalent bonds), as in Figure (1-11), and according to the physical appearance, they are classified into (microballs, fibers, powders, and films).

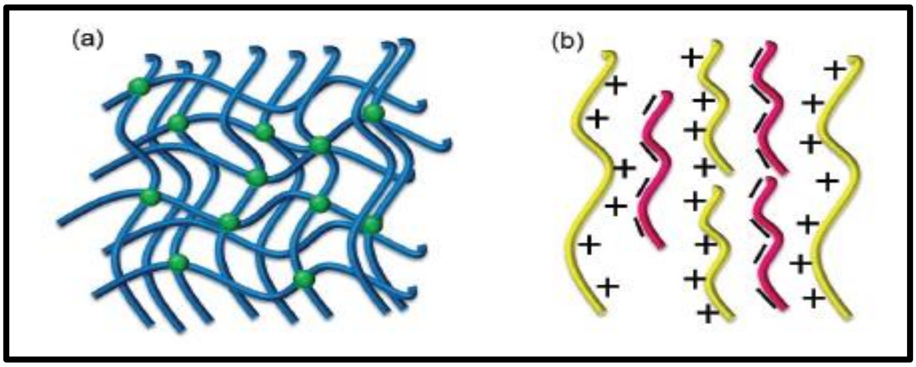


Figure (11-1) (a) Chemical gels (b) Physical gels.

Adsorption: is the adhesion or accumulation of atoms, ions or molecules (liquid or gaseous) on a solid surface, or it is a physical or chemical association of material molecules at the active sites of the surface by weak van der Waals forces or by forming chemical bonds with the active sites on the surface. The material that accumulates on the solid surface is called the adsorbate and the surface on which the adsorbate collects is called the adsorbent surface, as in Figure(1-13)

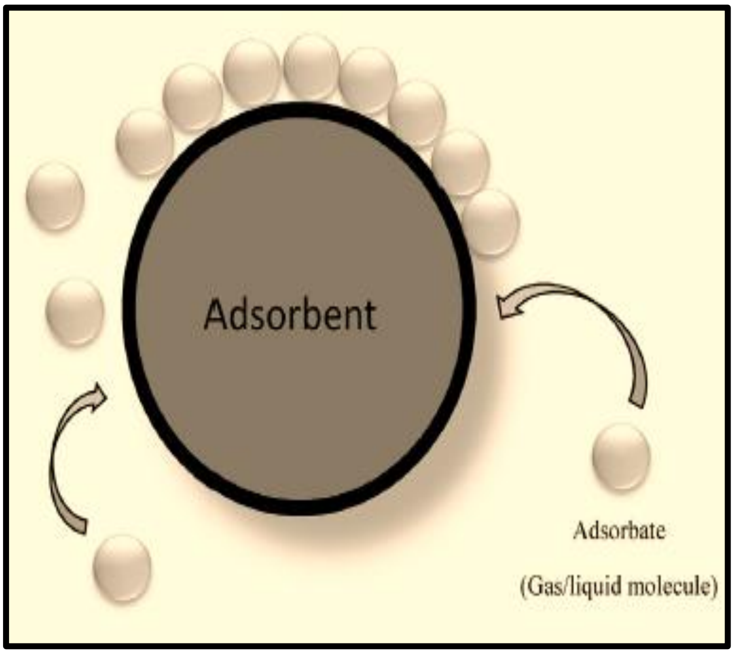


Figure (13-1) Adsorption process.[55]

The occurrence of adsorption may be limited to one layer of surface molecules and is then called Uni-molecular Adsorption, and at other times it extends to include several molecular layers and is then called Multi-molecular Adsorption.

The reason for the occurrence of the adsorption phenomenon is the presence of unsaturated active site residues on the adsorbent surface due to the attachment of an insufficient number of particles to the surface and the appearance of unbalanced molecular forces on the solid surface. To get rid of these forces, the solid surface tends to attract and retain the particles.

In this context, the process opposite to the adsorption process is called desorption, which is the process of separation of the particles collected on the adsorbent surface and their return to their original surroundings. Desorption occurs in the event of a temperature rise to a degree sufficient to break the bonding forces between the adsorbent surface and the adsorbent materials, as in Figure.(14-1)

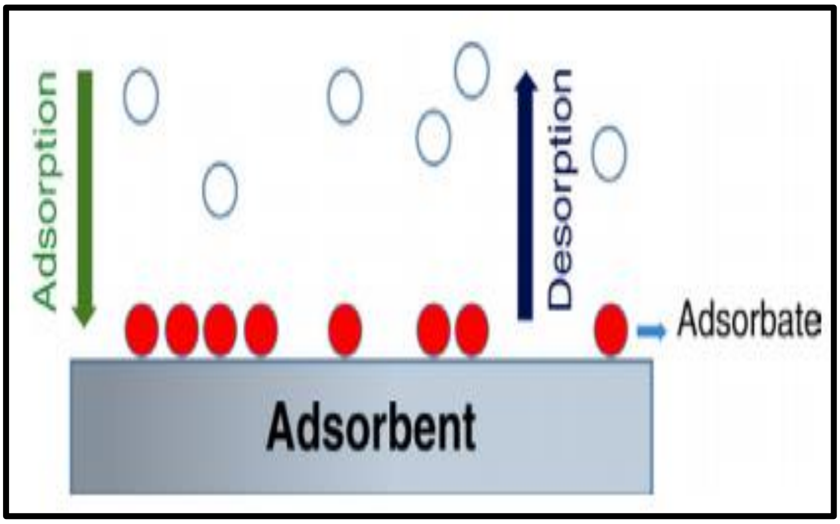


Figure (1-14) The difference between adsorption and absorption [6].

Adsorption differs from absorption in that it is a surface phenomenon, while absorption is the entry of molecules of the adsorbed substance into the adsorbent substance and their spread within it, and adsorption precedes absorption. When adsorption and absorption occur together, the process is called Sorption, as in Figure
.(15-1)

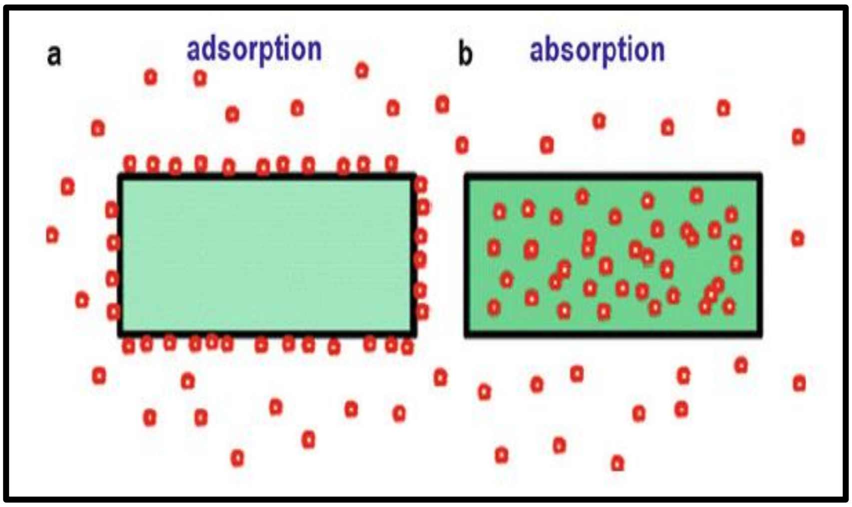


Figure (1-15) Adsorption and absorption [59].

Types of adsorptions:

Adsorption is of two types: physical adsorption and chemical adsorption, as in Figure-16)

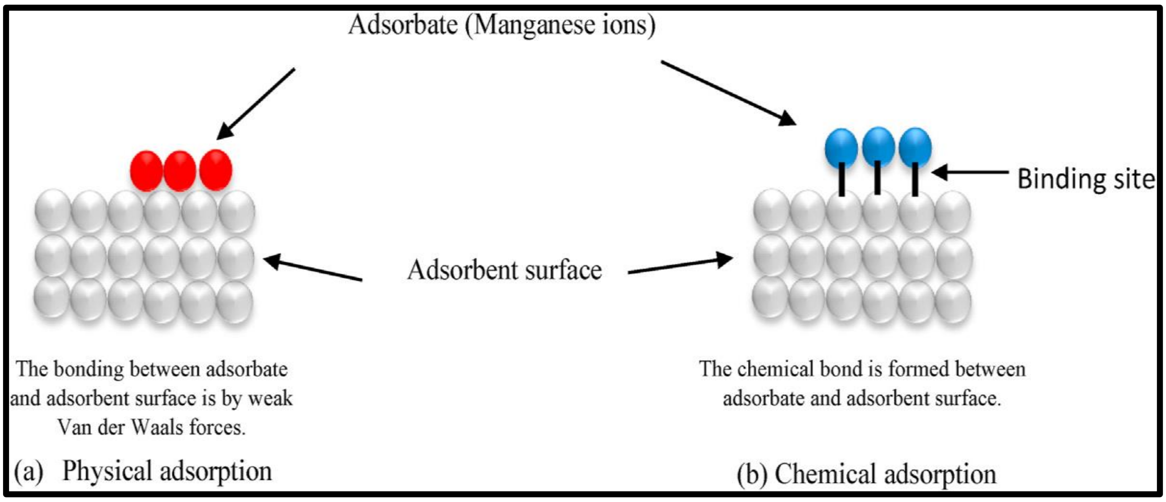


Figure (16-1) Types of adsorption (a) Physical adsorption (b) Chemical adsorption.

Table (1) shows the differences between physical adsorption and chemical adsorption.

Table (1) Differences between chemical and physical adsorption

physical adsorption	Chemical adsorption
Heat of adsorption is less than (40 kJ.mol-1).	The heat of adsorption is higher than (80 kJ.mol-1).
It does not require any activation energy to occur.	It requires activation energy to occur.
Single or multilayer.	Monolayer.
It occurs at normal or low temperatures.	It occurs at temperatures above the boiling point of the adsorbent.
non selective	Selective adsorption.
There is no transfer of electrons and the adsorbed particles are bound to the adsorbent surface by weak physical forces.	It involves the transfer of electrons between the adsorbed particles and the adsorbent, which leads to the formation of chemical bonds between the adsorbent and the adsorbent.
Fast and reverse.	Slow and non-reversible.

Adsorption from solution:

Since the solution consists of two or more substances, which are the solute and the solvent, it is not easy to carry out adsorption of the solute on any absorbing surface, because the components of the solution compete for the active or effective sites on the absorbing material. The occurrence of this adsorption depends on two factors: the nature of the interactions that occur between the components of the solution, as well as the nature of the interactions that occur with the absorbing material. An important example of adsorption from the solution is the use of activated carbon to get rid of colored materials in solutions such as sugar solution

Adsorption from the solution includes several main steps:

(1) The spread of the adsorbed particles on the absorbing surface.

(2) Adsorption of the adsorbed particles and their association with the absorbing material.

(3) Breaking the bonding forces between the reactants and forming new bonds. (4) The reactants leave their sites on the absorbing surface to enter the pores of the absorbing material.

Factors affecting adsorption:

Temperature

Adsorption is generally exothermic, so an increase in temperature leads to a decrease in the rate of adsorption because an increase in temperature causes an increase in the kinetic energy of the adsorbed particles, which increases the possibility of separation of the adsorbents, and vice versa.

Acidic function pH

Adsorption from the solution is affected by a change in the pH of the solution, as a result of the effect of the acidic function on the adsorbed particles and the adsorbent. This effect results from the competition of the adsorbed particles, the positive hydrogen ion (H+) and the negative hydroxide ion (OH-) to interfere with the adsorbent, and thus an increase or decrease in the adsorption capacity occurs.

Ionic strength:

The rate of adsorption changes with a change in the ionic strength of the solution. The increase in ionic intensity means an increase in the competition between the adsorbed particles and the added salt ions to bind to the active sites of the adsorbent, i.e. it is inversely proportional to the ionic intensity.

Nature of the adsorbent:

The nature of the adsorbent surface and its physical and chemical properties affect the efficiency of the adsorption process, as each of the following affects: the chemical composition of the adsorbent in terms of the presence of polar or nonpolar groups, the area of the adsorbent surface, the size of the surface pores, and the available number of active sites.

Nature of adsorbate particles:

The physical properties of the adsorbent particles affect the adsorption process, as increasing both the molecular weight and the size of the adsorbed particles leads to an increase in the adsorption capacity, and the more the solubility of the adsorbents in solvents increases, the adsorption capacity decreases. The chemical composition of the adsorbents also affects, as the more functional groups of the adsorbents, the more their association with the surface of the adsorbent increases

Concentration of adsorbate:

The adsorption capacity increases with increasing adsorbate concentration until reaching equilibrium, as a result of the increased diffusion of adsorbed particles on the adsorbent surface, and thus requires a longer time to reach equilibrium.

Equilibrium time

It is the time required for equilibrium to occur between the adsorbed particles and the adsorbent, at which the speed of the adsorption and desorption processes is equal, as all the active centers of the adsorbent surface are associated with the adsorbed particles, and after that there is no decrease in the solution concentration.

Solvent effect and Traube's Rule.

The solvent affects the adsorption, as its molecules compete with the adsorbent particles to occupy the active sites of the adsorbent surface. This depends on the composition of the solution components and the adsorbent material, as the solubility and polarity of the adsorbents affect the adsorption capacity. The lower the solubility of the adsorbent particles in the solution, the greater the possibility of their adsorption. 1-8-4 Adsorption isotherms. Adsorption isotherm represents a relationship that links the amount of adsorbed material (Qe) with the equilibrium concentration (Ce) in the solution or with the pressure of the adsorbed particles in the gaseous state, at a constant temperature. Adsorption isotherms were classified by (Giles and his group) into main classes, which are (S, L, H, C), and there are secondary classes within them, which are 1), 2, 3, (Max.

Class (S): The isotherm of this class takes the form of the letter S, and in it the adsorbed particles are directed or connected either obliquely or perpendicularly to the surface of the adsorbent material.

Class (L): This class is concerned with the Langmuir model of adsorption, the adsorption of this class is monolayer, and in it the adsorbed particles are directed horizontally to the surface of the adsorbent material.

Class (H): This class is concerned with the case of a high attraction between the adsorbed particles and the adsorbent surface, and this occurs either in the case of large adsorbed particles such as polymer molecules or When the solution is dilute.

Class (C): This class is in the form of a linear curve, formed as a result of chemical adsorption, and there is a fixed barrier between the adsorbent and the solution on one side and between the adsorbed particles on the other side.

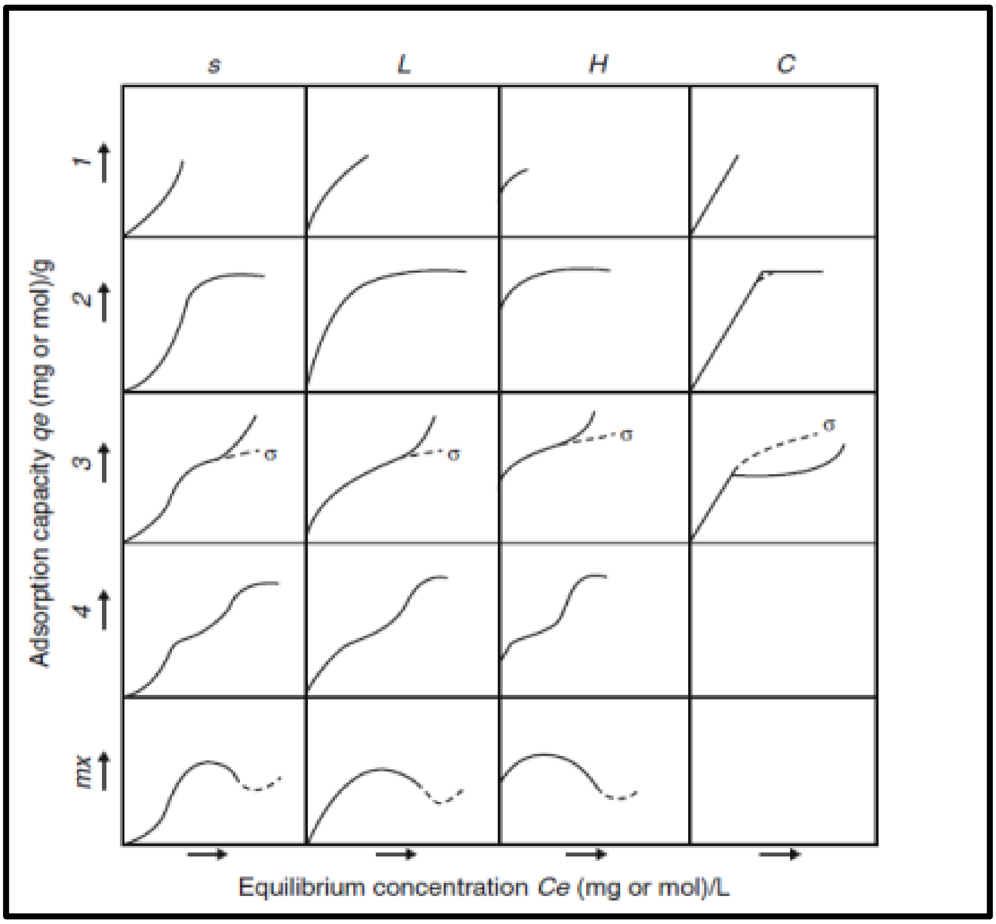


Figure (7) Adsorption isotherms according to Giles classification.

CONCLUSION

This study investigates the application of thiazole complexes to remove various harmful textile dyes, examining factors like adsorption efficiency, dye classification, and chemical composition. Key findings demonstrate effective removal mechanisms driven by thiazole's unique properties, including adsorption behavior and chemical bonding, making thiazole complexes promising for dye pollution mitigation in wastewater treatment.

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