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Entitled:

Utilization of Prickly Pear Peels as Agricultural Waste for the Removal of Organic Pollutant from Aqueous Solution

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Dedication

Hours passed and the days passed and I was building my dream a lofty joy in the sky of my world and here my days are towards glory and I decorate my painting with the most beatiful to the one who was pushing me forward to get what I wanted to my first school in life my dear father may god prolong is life to the one who taught me that deeds are done with patience and persistence to the one who gave in front of her feet to the one who gave me her blood soul and life with love and determination for a more beautiful tomorrow To the cadles of my life to the pure tender hearts and innocent souls to the winds of my life my sisters and brothers And to every one who is dear to my heart the hear reminds them and my pen did not mention them to those who share with me my trouble and my misery in the note my friends with whom

I taught me to study.

Ageuib Mouna

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Abstract

Nowadays, ecosystems still suffer from the dire reflections of dye pollutants. In this study, an eco-friendly and zero-cost was prepared using raw prickly pear peel. The surface and physicochemical properties of PPP-Raw were evaluated by BET, SEM-EDX, FTIR, and pHpzc analyses. Surface analysis revealed that PPP-Raw possesses an enriched composition of nucleophilic functional groups, including OH, NH, and COOH in an alkane medium, leading to diversity in the adsorption mechanism, involving electrostatic attraction, hydrogen bonding, and $\pi - \pi$ interactions. This diversity significantly contributed to reaching a maximum adsorption capacity for MV 2B of 569.6 mg/g. The change in thermodynamic state functions ΔG, ΔH, and ΔS suggest the possibility of physisorption simultaneously and indicate the exothermic and spontaneous characters of the adsorption of MV 2B dye on PPP-Raw with negative values of ΔH and ΔG. The findings of this research will further urge the current management of the water environment to embrace the use of raw prickly pear peels as a natural resource adsorbent without any chemical treatments in the remediation of organic dye-contaminated wastewater.

Keywords: Adsorption, Response surface methodology, Prickly pear peel, MV 2B dye.

الملخص

في الوقت الحاضر، لا تزال النظم البيئية تعاني من الانعكاسات الرهيبة للملوثات الصبغية. في هذه الدراسة، تم تحضير منتج صديق للبيئة وبدون تكلفة باستخدام قشر التين الشوكي الخام. تم تقييم الخصائص السطحية والفيزيائية والكيميائية لـ PPP-Raw بواسطة تحليلات BET ، SEM-EDX ، FTIR وpHpzc. كشف التحليل السطحي أن PPP-Raw يمتلك تركيبة غنية من المجموعات الوظيفية المحبة للنواة، بما في ذلك OH، NH وCOOH في وسط ألكاني، مما يؤدي إلى التنوع في آلية الامتزاز، بما في ذلك الجذب الكهروستاتيكي والترابط الهيدروجيني وتفاعلات $\pi - \pi$. وقد ساهم هذا التنوع بشكل كبير في الوصول إلى أقصى قدرة امتصاصية لـ MV 2B تبلغ 569.6 ملغم/غم. يشير التغير في وظائف الحالة الديناميكية الحرارية ΔG ، ΔH و ΔS إلى إمكانية الامتصاص الفيزيائي في وقت واحد ويشير إلى الخصائص الطاردة للحرارة والعفوية لامتصاص صبغة MV 2B على PPP-Raw مع قيم سالبة لـ ΔH وΔG. ستحث نتائج هذا البحث الإدارة الحالية للبيئة المائية على تبني استخدام قشور التين الشوكي الخام كمورد طبيعي ممتز دون أي معالجات كيميائية في معالجة مياه الصرف الصحي الملوثة بالصبغة العضوية.

الكلمات المفتاحية: الامتزاز، منهجية سطح الاستجابة، قشر التين الشوكي، صبغة MV 2B.

.

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LIST OF SYMBOLS and ABBREVIATIONS

SEM	Scanning electron microscope
EDX	Energy-dispersive x-ray spectroscopy
FTIR	Fourier Transform Infrared
RSM	Response Surface Methodology
BBD	Box Behnken design
q_e	Adsorption capacity at equilibrium
q_t	Amount of dye adsorbed per unit of adsorbent
R^2	Correlation coefficient
K_L	Langmuir constant
K_f	Freundlich constant
K_T	Temkin constant
C_0	Initial concentration
C_e	Equilibrium concentration
t	Time
V	Volume of adsorbate
W	Weight of adsorbent
PFO	pseudo-first-order
PSO	pseudo-second-order

GENERAL INTRODUCTION

- **Background of the study**

Pollution is considered one of the major problems facing humans and the environment, especially after the technological development that has accompanied urbanization [1]. It occurs in various forms, whether in water, air or soil, as a result of the presence of some harmful organic or inorganic substances, or due to an increase or decrease in the proportion of some basic components present in the environment above their natural proportion. This occurs as a result of human interventions or some natural phenomena[2]. Scientists and specialists in the field of pollution have been particularly interested in water pollution, and it is not surprising that the studies that dealt with this topic were much larger than those that dealt with other branches of pollution [3].

Interest in actively studying the behavior of environmental dyes began after news circulated about the potential danger of these materials[4] . This interest increased after realizing the fact that many of the raw materials used in the preparation of these dyes are essentially carcinogens such as benzidine, aniline and other amino compounds and colorants that can be reconstituted as a result of some biological reactions or degradation of these dyes[5]. Therefore, increasing their presence in wastewater is undesirable and unlikely, and it is best to remove these substances from the water before sending them to the environment, not only for environmental aesthetic reasons, but also because of their toxicity and short- or long-term damage to the environment and humans. [6]. Dyes are considered one of the materials that pollute water sources, and the reason for this is their widespread use in various industries. Including paper printing, Cosmetics, printing, food industry, leather, and the textile industry is considered the most consuming of it[7].

Textile industries discharge large amounts of wastewater containing synthetic dyes. These discharges pose a real risk to humans and the environment due to their unstable chemical uses and low biodegradation capacity. Technologies for removing organic pollutants from organic solutions are ineffective, too sophisticated and too expensive for developing countries. Therefore, there is a need to look for other effective and inexpensive ways to mitigate the negative effects of wastewater contaminated with organic pollutants on public health and the environment. Wastewater must be carefully treated before being discharged into main water sources[8].

Many physical and chemical processes have been developed to remove industrial dyes from wastewater, such as coagulation and concentration, oxidation and ozonation, membrane separation, photolithography and biological processes[9; 10]. However, these methods suffer from several drawbacks, including incomplete removal of organic contaminants and investment costs.

Adsorption is one of the most effective techniques and has been used for a long time in the water and wastewater industries to remove organic materials and inorganic contaminants, due to its ease of handling and reusability[11]. Activated carbon is considered one of the most effective materials. It is an adsorbent material for treating polluted water, whether organic or inorganic. It has a high adsorption capacity due to its large surface area[12; 13], But it is still cumbersome, and its use is limited due to its high cost[14]. Therefore, water treatment by adsorption with natural materials addresses this limitation in an effective and economical manner. Prickly pear peel is an interesting adsorbent, due to its low cost and availability in nature[15; 16].

- **Problem Statement**

One of the most alarming issues facing humanity today is water pollution resulting from increasing industrialization. Most of the dyes that are discharged into water bodies without treatment due to development may pollute the water. Since it produces high quality treated effluent[17].

It has been demonstrated that adsorption is an effective method for eliminating color from wastewater. Natural biomaterial waste for decolorization has received a lot of attention lately, similar to prickly pear peels, because it is inexpensive, readily available, and biodegradable[15; 16].

- **Research Objectives**

This study focuses on preparing an effective adsorbent for treating textile waste contaminated with organic pollutants. In this regard, adsorbents have been completed, which have many advantages such as their availability and low cost because they do not require any treatment. In our work, we chose methylene violet 2B (a cationic dye) as a model dye. Therefore, the main objectives of the current study are:

✓ Preparation of a new natural and vital adsorbent using raw prickly pear peels.

✓ Study of the efficiency of the adsorbent In the adsorption of methylene blue dye from aqueous solutions.

✓ Determine the best factors that affect the adsorption of this dye, such as contact time, initial dye concentration, temperature and pH.

✓ To characterize the adsorbents using scanning electron microscopy (SEM), Fourier-transform infrared (FTIR) spectroscopy, and energy-dispersive x-ray (EDX) spectroscopic techniques.

✓ Isotherm modeling, kinetics and thermodynamic study to evaluate adsorption behavior.

✓ Evaluation of the performance of the prepared adsorbent to remove MV 2B dye from aqueous solution by the response surface method (RSM).

- **Significance of study**

Raw prickly pear peels can be converted into an adsorbent in an environmentally friendly and cost-free manner to efficiently remove pollutants. Which has promising prospects in this field due to its economical and uncomplicated preparation method in the absence of chemical treatments. This adsorbent shows a porous structure and a reasonable surface area. It is insoluble and similar to a sponge, whose task is to retain and automatically capture pollutant molecules, which shows high effectiveness in adsorption of pollutants. of water.

- **Thesis Layout**

This note contains four chapters, which we mention in succession:

General Introduction: A general introduction explaining the content of the research and the research problem, mentioning its objectives, as well as its importance, and ending with the division of the memorandum.

Chapter 1: It includes a theoretical study on pollution, dyes, techniques and methods for treating water from pollutants and is completed with an overview of adsorption.

Chapter 2: In this chapter, we discussed the methods of preparing adsorbents and adsorbents. And searching for the optimal adsorption process parameters by BoxBehnken design

Chapter 3: This chapter presents the research results. The preliminary study is discussed first, followed by characterization, optimization and modeling of the selected adsorbents. The reaction mechanism is also discussed.

At the end of this work was general conclusion which summarizing the main of obtained results and offering some recommendations for future work

CHAPTER 1

LITERATURE REVIEW

1.1 Introduction

This chapter is contained at three main parts which are the pollutant , technique of treatment this pollutant ,and some researchs. the first part describes about a brief history of dyes, types, and their toxicities .The second part also explains with the best low cost technique for removing the dye which is the adsorption.

1.2 pollution

Water pollution can be defined as the introduction of harmful substances or factors (physical, chemical or biological) that lead to its contamination and change its natural characteristics, causing harmful effects on aquatic life and on those who consume the water [18], It can occur as a result of the discharge of wastewater from factories or homes without treatment, the leakage of harmful chemicals from farms or industrial facilities, and plastic waste, oils and spoiled organic materials can also be a source of pollution [2]. Some of these sources are shown in the figure : 1.1

Figure 1.1: Various sources contribute to water pollution

1.2.1 Types of Water Pollution

1.2.1.1 Biological pollution

A large number of microorganisms can multiply in waters that serve as natural habitats or as a simple means of transport of these microorganisms.

These are the main pathogenic organisms that reproduce in water: bacteria, Viruses, parasites, fungi[19].

1.2.1.2 Physical pollution

This type of pollution results in particles of very diverse sizes and materials being present in the water, giving it a cloudy character[19].

We also distinguish between stable substances (heavier than water itself) and floating substances (lighter than water itself) and inseparable substances (having the same density as water).

La pollution physique fait référence à un autre type de pollution, comme la pollution thermique résultant de Une augmentation de la température entraîne une diminution de la teneur en oxygène dissous ainsi qu'une diminution de... Gaz de fonte et contamination radioactive là où l'eau naturelle peut être radioactive D'origine naturelle ou artificielle (énergie nucléaire)[20].

1.2.1.3 Chemical pollution

Chemical pollution of water results from the release of certain toxic mineral substances in watercourses, for example: nitrates, phosphates, ammonia and other salts, as well as metal ions, These substances have a toxic effect on organic materials and make them more toxic dangerous[19].

Chemical pollutants are currently classified into five categories: Unwanted chemicals, pesticides, related products, Detergents, dyes and other toxic elements[21].

1.2.2 Causes of water pollution

In terms of public health around the world, environmental pollution is a major concern. Recently it poses a huge threat to biodiversity and humans. The release of industrial liquid waste into the environment also affects the quality of soil, air and water [22; 23], Hence the deterioration in water quality caused Human activities and industrialization result in water pollution. With the increasing demand for fresh water, the discharge of notorious pollutants has led to an increase in the number of water pollution incidents [24; 25].

1.2.3 Sources of water pollution

Water pollution may result from various sources, the most important of which are:

1.2.3.1 Domestic sewage

The majority of the domestic sewage that is dumped into rivers is untreated. Water pollution is caused by the toxicants, solid debris, plastic litter, and bacterial pollutants found in domestic sewage. The main cause of water pollution is various industrial waste that is dumped into rivers untreated[26].

1.2.3.2 Population growth

Increasing population is creating many issues but it also plays negative role in polluting the water[27], Increasing population leads to increase in solid waste generation [28], And the questioner The waste is discharged into water bodies. It is also polluted by human waste, It also contains a large number of bacteria that are harmful to human health [29].

1.2.3.3 Pesticides and fertilizers

Pesticides are used to kill various bacteria, diseases, and germs. They also contain chemicals that directly pollute the environment and affect water quality if pesticides are in excess. In terms of quantity or mismanagement, it will be dangerous for the agricultural ecosystem [30; 31].

1.2.3.4 Industrialization

Ground and surface water pollution is caused by hazardous substances released by companies. The type of pollutants varies depending on the industry. When toxic metals enter the water, they reduce the quality of the water [27]. In fact, they are becoming more massive and diverse as well as more insidious. Due to the significant difference between the different versions, a unique study must be carried out for each type of industry: therefore, it is necessary to have a comprehensive understanding of the circuit and manufacturing processes for both agents and products. It is clear that improper handling of liquid waste disposal leads to unfavorable changes in the receiving environment as well as extremely dangerous pollutants. Among the basic industries that contribute to pollution, the textile sector occupies an important enough place to be taken into consideration[32].

1.2.3.4.1 Brief description of the textile industry

The textile industry brings together a wide range of professions along a transformational chain that starts with fibrous materials and ends with fully or semi-manufactured goods.

She offers the benefit of representing a whole chain that goes from raw materials to finished goods that are delivered to customers.

Materials that can be made into covers, ropes, textiles and threads are known as textile fibres. This may appear at the animal, plant, mineral or chemical level[32].

1.3 Dyes

These are substances used to give color to other materials. Dyes are used in a wide range Applications particularly in the food industry, which are generally organic compounds, Natural or artificial has the property of coloring the support applied to it always. It is characterized by its ability to absorb light radiation In the visible spectrum (380 to 750 nm). Pigments are made up of a group of chromophoric groups. auxochromes . They are used to color various materials such as: textiles, leather, paints, fibers, paper, plastics, food products, printing, paints and even agricultural colors. Pigments contain small particles They absorb and reflect light rays in such a way that we see the color they represent [32; 33].

chromophoric: It determines color, allows dyeing of materials, and is responsible for its production.

auxochromes: It determines the intensity of the dye and acts as a complement to the chromophore, increasing its solubility in water and increasing its affinity. In order to stabilize the fibers.

1.3.1 History of dyes

Dyes have been applied for more than 4,000 years, as humans used natural materials to add colors to fabrics. Food, cosmetics as well as paper printing etc. The colors used were of natural plant, animal and mineral origin[7].

In 1856, Perkin discovered the first artificial dye (muffin)[34]. The big change in dyes came after the discovery of mouven by William Henry Perkin in the same year while trying to find a way to synthesize quinine, a drug used to treat malaria. Therefore, Henry Perkin, in his attempt to synthesize quinine, produced a new type of gel dye[35].

In 1871, the synthetic organic dye was produced when Wolff prepared picric acid by treating the natural indigo dye with it. Nitric acid. Since then many new chemical dyes have been added to the list of dyes[7]. It also completely replaced almost natural dyes at the beginning of the twentieth century, and its industry witnessed a major boom with the discovery of new chemicals and technologies.[36].

1.3.2 Sources of dyes

The first dyes used by humans were natural dyes and they can be divided They are divided into three categories: mineral, animal and vegetable dyes.

1.3.2.1 Natural dyes

The first dyes used by humans were natural dyes and they can be divided They are divided into three categories: mineral, animal and vegetable dyes.

a- vegetable dyes: Historically, plants have been used to extract most natural dyes from Various plant parts including roots, stems, leaves, twigs, bark, wood, flowers, fruits, peels and the like serve as a natural dye source. Among the plants from which dyes are extracted is the Rubia plant, Saban wood, turmeric, annatto, onion, saffron, pomegranate as well as Kamala plant[37].

b- Animal dyes: Insects and molluscs are the main source of natural dyes of animal origin Among them are: cochineal beetles, scale insects, and oysters[38].

c- Mineral dyes: Natural mineral pigments such as azurite, talc, coal black, malachite, red ochre, yellow ochre, raw sienna, and ultramarine blue have all been utilized as coloring agents. Except for red ocher, which the monks used, it was primarily utilized in paintings and murals along with glue as a binder. to dye their garments[38].

1.3.2.2 Synthetic dyes

Artificial colors are obtained from chemical reactions (tartrazine, quinoline yellow. etc). Most of these dyes are made primarily from petroleum products, especially gasoline and its derivatives Thanks to (naphthalene, anthracene ..etc), they are increasingly used in the dye and textile industries. Ease of synthesis and speed of production[37].

1.3.2.3 Use and application of dyes

-Brick making: paintings.

-In Printing and Paper Industries.

-Agricultural industry (food colorings).

-Pharmaceutical industry.

-Plastics industry.

-Textile industry.

1.3.2.4 Toxicity of dyes

The release of wastewater containing dyes into aquatic habitats is a significant issue. These materials are actually recognized for their toxicity [35] , which is mostly caused by their huge molecular weights and intricate molecular architectures, which allow them to withstand both accumulation and biodegradation. The most poisonous hues are thought to be diazo ones. Azo dyes have been shown in numerous studies to cause cancer in people. The primary cause of this impact is the enzymatic or chemical breakdown of azo linkages, which produces aromatic amines. The body can absorb these aromatic amines through the skin, lungs, digestive tract, and tract, and they can be eliminated by urine [39].

Because it reduces the oxygen and diffusion in this environment associated with this toxicity, animals, plants, and other microbes living in these waters may become infected. Because the degree of toxicity shown by different chemicals varies. For this reason, they are able to live in this environment for long periods of time, causing serious disturbances to various natural processes that control plants (such as by inhibiting the growth of aquatic plants and spontaneous purification of waterways) and animals (by inhibiting the growth of aquatic plants and spontaneous purification of waterways). Killing a certain class of fish and organisms). Bacteria[40].

1.3.3 Classification of dyes

The color and properties of dye molecules depend primarily on their chemical composition. can be classified Depending on the chemical composition (functional groups), color, or application elements [41]. And because there is Special complications in the nomenclature of these dyes in terms of their chemical formula. Recently, reliance has been placed on Classification of dyes using their molecular charge when dissolved in aqueous applications. They are broken down into pigments Non-ionic (dispersed dyes), cationic (basic dyes), while anionic (dyes Direct, reactive and acidic) [42].

1.3.3.1 Non-ionic (dispersed) dyes

These dyes are applied to hydrophobic fibers and are often nonionic, soluble, or slightly soluble in water. Water-based dispersions are usually applied to polyester, although they are also useful on nylon, acrylic and cellulose acetate fibres[35], While azo structures serve as the basis for most disperse dyes, the colors are violet and blue It is often extracted from anthraquinone compounds[43].

1.3.3.2 Anionic dyes

Anionic dyes contain negative ions due to the presence of excess (OH^-) ions in the aqueous solution. They are water-soluble dyes and include acid, azo, direct and reactive dyes. Reactive dyes bind to their substrates via a chemical reaction that forms a covalent bond between the dye molecule and Those for fiber[33].

A- Direct dyes

They are anionic dyes that are not acceptable in water and have a strong affinity for cellulosic fibers when added to an aqueous solution with electrolytes. This family of colors often includes polyazo compounds as well as some types of stilbene, phthalocyanine and oxazine. These dyes are used For coloring paper, leather, cotton, rayon, and to a lesser extent nylon[44].

B- reactive dyes

Most reactive colors are azo or metallocene dyes, in addition to anthraquinone and phthalocyanine dyes, which are often used for blue and green. The chromophore group and the reactive chemical function are included Reactive dyes create a covalent bond with the fiber[45]. These dyes are often used for cotton and other cellulosic materials, although they can also be used for cotton and other cellulosic materials Use it sparingly on nylon and wool[44].

C- acid dyes

These dyes mostly belong to the chemical classes of azo, anthraquinone, triphenylmethane, Azine, xanthine, nitro, and nitroso [34],It is used to some extent for paper, leather, inkjet printing, food and cosmetics. It is also used in the manufacture of nylon, wool, silk and modified acrylic. It usually dissolves in water[44].

D- Vat dyes

Because cuvee dyes are insoluble, they must be reduced to leucoderivés using a process called alcaline reduction. The final step in the coloring process is the in situ reoxydation of the initial insoluble Dye. Renowned for their strong resistance to deteriorating chemicals, curing dyes are still used, similar to indigo, to tint denim or jean clothing[46].

1.3.3.3 Cationic dyes

Cationic (basic) dyes are dyes that contain Functional groups that can dissociate into positively charged ions in aqueous solution to The most prevalent cationic functional group is the anionium group, so most cations are (N^{+}) [47], They are water soluble and are highly visible in water even at very low levels concentration. Cationic function is found in various types of dyes such as cationic azo dyes , anthraquinone, di- and tri-arylcarbenium, phthalocyanine pigments[33] and Methyl violet 2B[48].

a-1 Methyl Violet 2B dye (MV2B):

Methyl violet 2B (MV2B) is a typical aromatic azo compound with the molecular formula shown in Table: 1.1, Its skeleton contains an extended conjugate system due to lack of positioning The electrons in the benzene, methyl, and amine ring are functional Combinations result in a wide range of high optics Absorption in the visible spectrum Spectral characteristics The nonlinear optical properties of the dye dissolved in it [49], and its molecular structure is shown. In figure: 1.2 as well (MV2B) is known as a cationic dye with high gloss and intensity [50], Soluble in water it gives a deep violet colour, although the colour MV2B is a dark green solid powder[48].

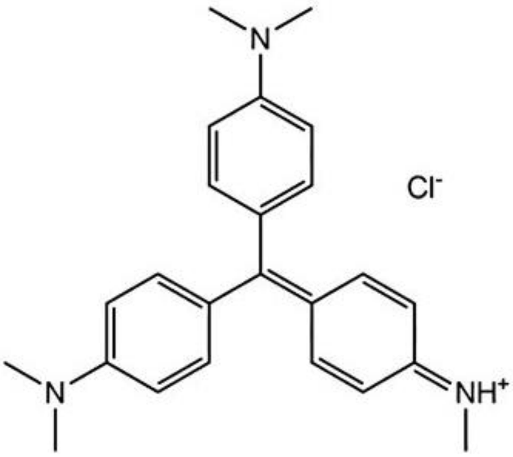

Figure 1.2: Chemical structure of the cationic dye methyl violet (MV 2B)

a-2 Harmful effects of MV 2B dye:

Reports have shown MV2B dye can hinder bacterial growth and photosynthesis of aquatic plants, and can be harmful through ingestion, inhalation, and skin contact[33]. Furthermore, it is a potential carcinogen. It causes severe irritation to the eyes, skin, and respiratory system in humans[48].

a-3 Physical and chemical properties of (MV2B:

table: 1.1 represents the main physical and chemical properties of Methyl Violet 2B (MV2B) dye[48; 49; 50].

Table 1.1: Physical and chemical properties of MV 2B

Name	**Methyl Violet 2B**
classifcation	Cationic dye
Molecular formula	$C_{24}H_{28}N_3Cl$
Chemical Name	N-(4-(bis(4- (dimethylamino) phenyl) methylene) cyclohexa-2,5-dien1-ylidene) methane aminium chloride)
Molar mass	393.959 (g/mol)
solubility	Water, Ethanol.
Melting point	137°C, 279°F, 410°K
The color	Violet
The appearance	Dark green solid powder

Figure 1.3: MV2B dye in solid and liquid states

a-4 Uses of (MV2B) dye:

MV2B dye may play a special role in Different areas of specialization such as applications in dye, Sensitive solar cells, DSSC, solar cells for energy switching, display devices, photo resistors, Nonlinear optical devices as well as gas sensors have been applied[49].

1.4 Techniques of water treatment

1.4.1 Water treatment

The term water treatment refers to the processes carried out to make treated water suitable for drinking, by removing odors and dyes, developing it, softening it, and removing its hardness. It is the process of converting urban water or wastewater into water that can be used for other useful purposes. So water or water is used. Sanitation operations have been carried out in several areas, and they are contaminated with many solid or dissolved foreign materials.

1.4.2 The goal of treatment

The process of disposing of wastewater in healthy ways is considered one of the necessary processes to provide a healthy environment for communities in accordance with international conditions and the latest engineering and scientific methods to keep the surrounding environment free of pollutants. The aim of this treatment is to prepare the water so that it is suitable for drainage on agricultural drains and for use in irrigation. Treatment is carried out to eliminate the causes of pollution in this water, whether organic or other, suspended or dissolved, by controlling, removing or analyzing them into harmless substances and gases, in addition to getting rid of harmful and disease-causing substances. organisms to trace the cause.

1.4.3 Pollutant removal techniques

Dye processing operations

During the different stages of dyeing in greater or lesser quantities

Dyes are lost due to the unavailability of surfaces to be dyed or colored.

Organic materials are toxic and require appropriate decontamination technology [51] Industrial effluent treatment due to lack of Homogeneity of their composition will always lead to the design of the processing chain

It ensures the elimination of various pollutants in successive stages

The first step is to eliminate uncontaminated materials

Soluble through pre-treatments (screening, sand removal, oil removal, etc.) or

Biological or physical and chemical treatments that ensure the separation of solid matter from liquid.

The most common disinfection techniques are in the second stage

It is divided into three types [52] Research is currently moving towards new, low-cost processes.

Use of new materials of biological origin such as agricultural and forest waste,

Microorganisms [53].

Water treatment technologies represented in figure : 1.4

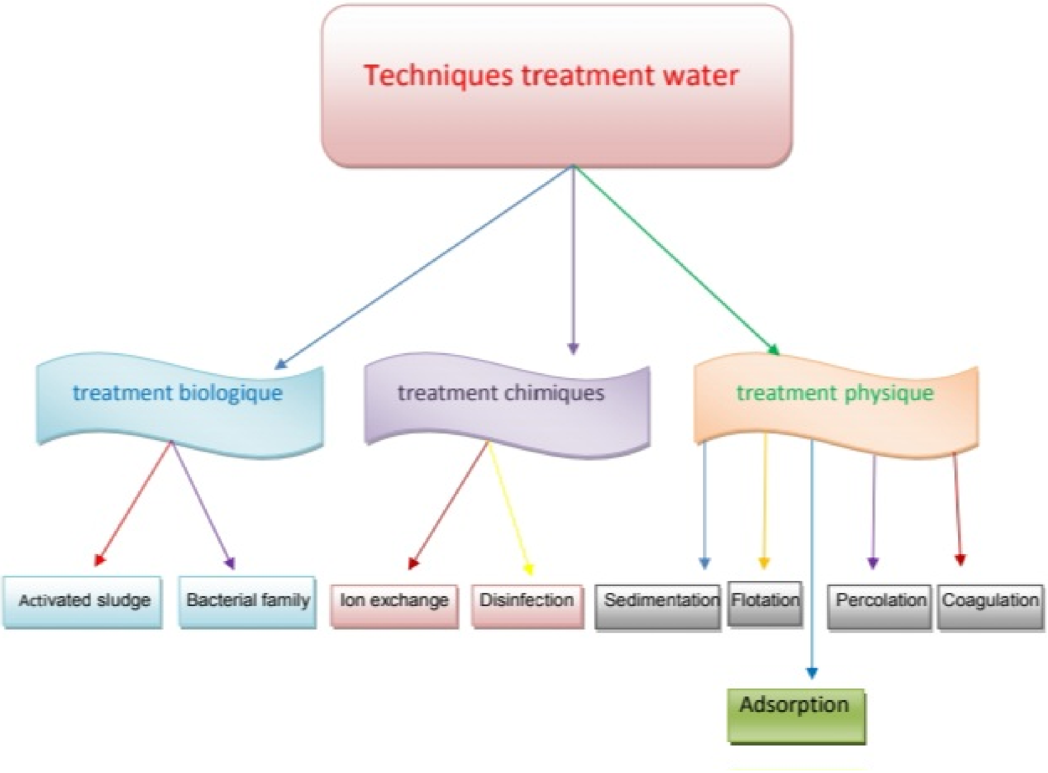

Figure 1.4: Water treatment techniques

1.4.3.1 Biological treatment

Biological treatment of wastewater is based on biological activities, through activated sludge processes that occur in aeration basins. Bacteria in wastewater play a role in the decomposition of pollutants dissolved in water [54]. Organisms that consume organic matter and concentrate it are called activated sludge. These processes exploit specific resistance mechanisms developed by microorganisms (bacteria, algae, etc.) that are capable of fixing and accumulating metals [55]. These organisms, also called biomass, which are of forest origin, are considered agricultural waste and among the most dangerous wastes for development. Biological purification processes are used in many countries [56]. One such process is biosorption, which corresponds to the use of biological materials to stabilize pollutants by adsorption.

1.4.3.2 Chemical treatment

Chemical dye removal methods are methods that use chemistry or its looks. Chemical techniques are usually more expensive when compared to biological and physical treatments. The chemical method has some drawbacks for dye removal, which make it unattractive for commercial use. It requires appropriate high-power reactor equipment, it requires large quantities [57], and requires specific procedures and high-power equipment [57]. in which the chemical dye is removed besides. , such as chemicals. There is another characteristic of this method: the generation of toxic secondary contamination resulting at the end of chemical dye removal. Dye removal poses additional disposal problems .

1.4.3.3 Physical treatment

Physical treatment is used to remove pollutants from contaminated water. It is an effective method for removing suspended solids, immiscible liquids and dispersed organic pollutants. Physical stain removal methods are usually clear and straightforward. It is accomplished by mass transfer mechanism and the physical methods of dye removal are adsorption, coagulation, flocculation, filtration and others. The physical method is more widely used in terms of efficiency and simplicity. This method requires the least amount of chemicals compared to biological or chemical dye removal methods[58]. This is not the way you approach life and therefore organisms are more predictable.

1.4.4 Adsorption

Adsorption is a process well suited to eliminate a very large amount of various toxic compounds in our environment. It is mainly used for water and air treatment[59]. Adsorption is a surface phenomenon in which gas or liquid molecules adhere to the solid surfaces of adsorbed materials as shown in figure : 1.5 according to different processes of varying intensity[60].

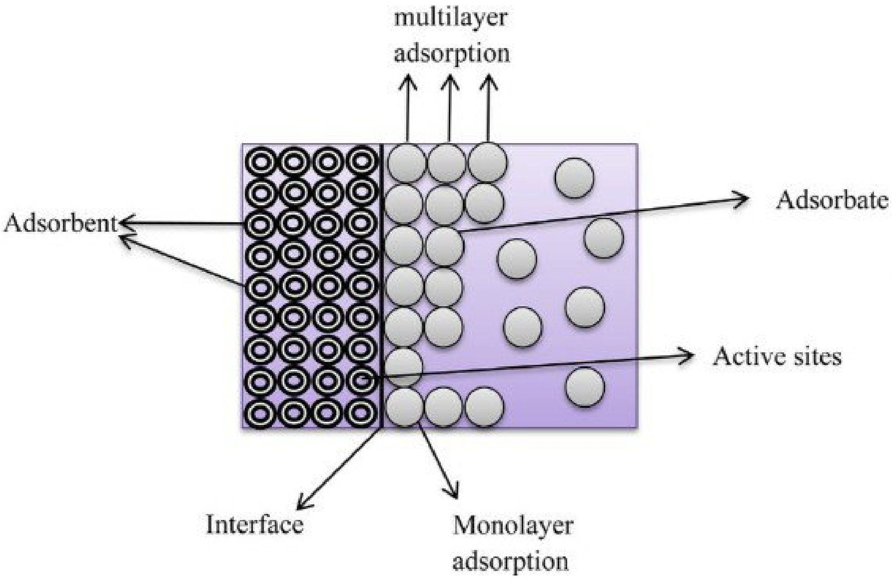

Figure 1.5: Mechanism of adsorption phenomenon

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1.4.5 Types of adsorption

The nature of adsorption depends on the interactions between adsorbent and adsorbent. Adsorption forces play an essential role in determining whether the adsorption is physical or not. It is difficult to precisely determine the type of adsorption that controls the mode. This may be a combination of chemical absorption and physical absorption[61]:

1.4.5.1 Physical adsorption

It is a process that attracts solid particles to the surface of another substance, a phenomenon that occurs at the molecular level. Physical adsorption is characterized by the fact that it relies on non-chemical interactions between solid particles and the substrate[62].In addition, weak interactions between molecules play an important role and are known as van der Waals forces. The speed of physical adsorption depends on the properties of the matrix and solid particles, such as active surface and molecular weight, as well as temperature and pressure [63].

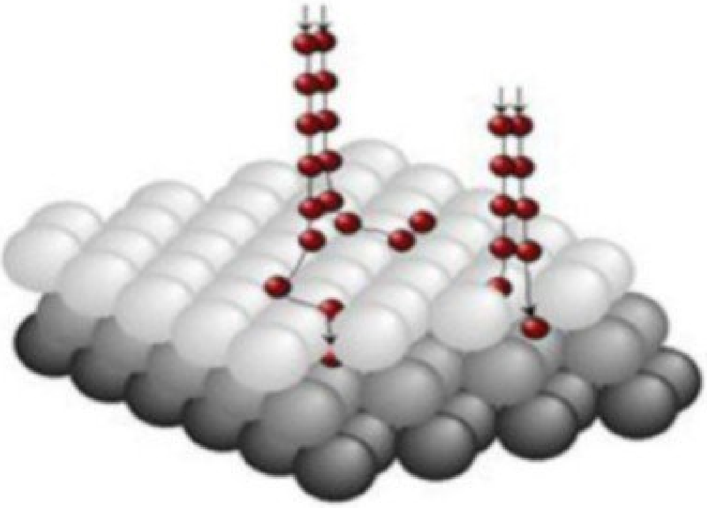


Figure 1.6: Physical adsorption

1.4.5.2 Chemical adsorption

It is the process of molecules interacting with each other to form ionic, covalent and internal covalent chemical bonds. This assembly between molecules occurs when electrons are exchanged between them[64].This type of adsorption is accompanied by much higher thermal changes than physical adsorption, as the amount of energy released as a result of chemical adsorption is more than 100 kJ/mol. This adsorption is also local, meaning that the molecule is able to move from its place of adsorption. It is non-reversible and limited to a single adsorption layer[65].

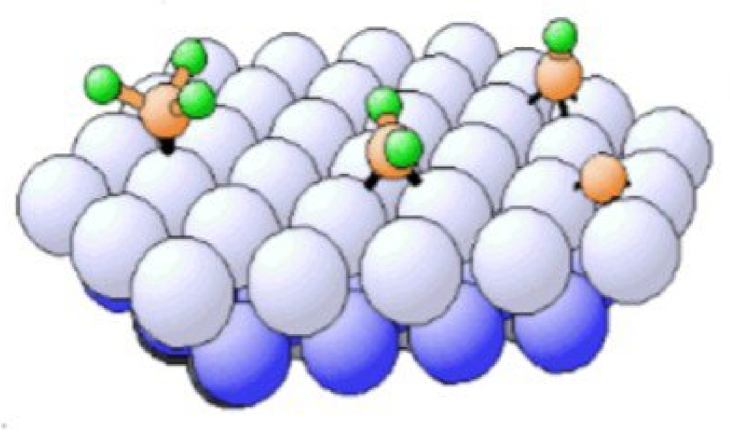


Figure 1.7: Chemical adsorption

Table 1.2: Comparison between physical adsorption and chemical adsorption

Properties	**physisorption**	**chemisorption**
Types of liaison	Van der Waals binding	Chemical bond
Temperatures of process	Relatively low compared to the boiling temperature of the adsorbate	Higher than temperature boiling point of the adsorbate
Individuality of molecules	The individuality of molecules is preserved	Destruction of individuality molecules
Desorption	Easy	Difficult
Kinetic	Fast, independent of Temperature	Very slow
Heat of adsorption	Less than 10 kcal/mole	Greater than 40 kcal/mole
Energies involved	Weak	High
Type de formation	Multi-layer training and single layer	Single-layer training

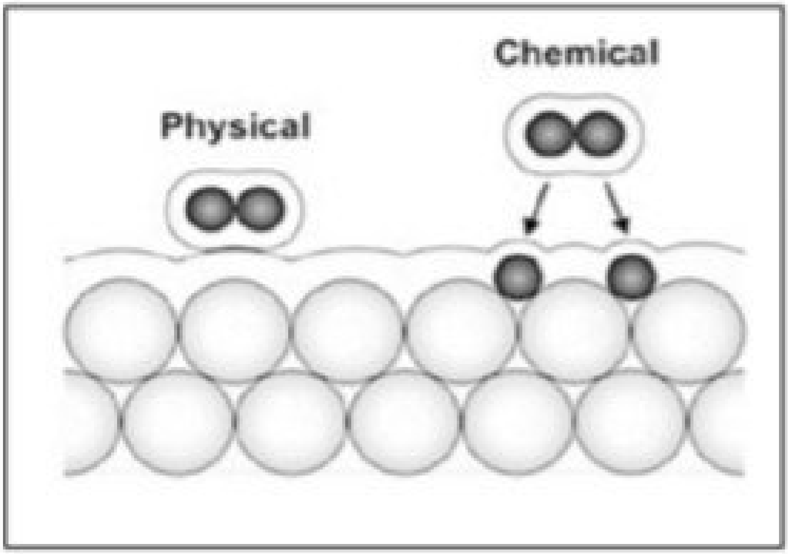


Figure 1.8: The occurrence of physical and chemical reactions on the surface

1.4.6 The importance of adsorption

Adsorption is a very important phenomenon in the development of many chemical reactions. They are used to trap unwanted particles in a fluid (gas or liquid) or retrieve valuable elements such as gold that is soluble in the liquid. Adsorption phenomena occur in catalysis and play an important role in the adhesion phenomenon between solid surfaces[66]. Adsorption is considered one of the most efficient and widely used techniques, as it is used in global environmental protection areas. Often, adsorbents are used as etch or carriers for catalysts, and sometimes they are used for gas separation or storage, liquid purification, pollution control, or respiratory protection. Therefore, adsorption is of great importance and is related to the surface properties and texture of fine powders such as pigments and cements[67].

1.4.7 Factors affecting adsorption

The adsorption process is affected by various factors. The transport of pollutants is determined by three physical and chemical phenomena. These phenomena include dynamic equilibrium between the two phases, adsorption kinetics, and competition between different adsorbents[68; 69]. Several factors influence these phenomena, such as the concentration of the contaminant in the solution[70], the hydrodynamic properties of the exchange, and the properties of the solution such as pH, ionic strength, and temperature. In general, adsorption at equilibrium increases as the temperature decreases, and heat is released during adsorption.

In addition, other factors such as solubility, structure, charge, and polarity of the contaminant affect the adsorption process [71; 72].

1.4.7.1 The nature of the adsorbent

The method of adsorption of materials varies according to each substance, as adsorption depends on the shape and size of the molecules. High molecular weight reduces diffusion, and dissolution capacity is inversely proportional to adsorption capacity. In other words, the less soluble the substance, the better the concentration of the adsorbent[73].

1.4.7.2 temperature

Adsorption is a comprehensive process consisting of several processes at the solid-liquid interface. It can be either exothermic or endothermic. Therefore, it depends on weather conditions. As a result, higher temperatures enhance the chemical reaction while lower temperatures enhance physical adsorption [74].

1.4.7.3 certain surface

In a liquid medium, sorbents act through their outer surface first. As for its inner surface, it must be accessed through pores that have a diameter larger than necessary to quickly absorb the gas. The greater the specific surface area, the greater the absorption capacity[75]

1.4.7.4 pH

The pH value is one of the vital factors that affect the mixing process. In particular, they affect the charge and ionization degree of miscibility, as well as the solubility of meta ions [76]. Where it affects everyone From the adsorbent structure and adsorbent structure, as well as to the adsorption mechanism. It plays an important role in the movement of metal ions. This is why the difference in pH of the medium leads to significant changes in the process Adsorption [77].

1.4.7.5 time

In the adsorption process, contact time is one of the main factors affecting it. The time required to achieve equilibrium and the type of isotherm must be determined. Therefore, the time required is the primary determining factor[73].

1.4.7.6 Shaking speed

As this factor works to distribute the adsorbed material on the adsorbent surface, the speed of shaking determines the maximum limit for adsorption [78].

1.4.8 Adsorption mechanism

Adsorption results from chemical and physical forces, in the case of solid and liquid adsorption, and this distinguishes We have several mechanisms for adsorption, including .

1.4.8.1 Vanderwaals forces

Adsorption is characterized by ion exchange and is of great importance in the adsorption of organic compounds, as it refers to the inter-dipole attractive forces that occur between atoms and molecules as a result of low-intensity electrical disturbances[79].

1.4.8.2 Coulomb forces

Electrostatic forces consist of differences in charge between the solid surface and the adsorbent. These forces appear mainly in the adsorption of inorganic ions and ionized organic molecules. This adsorption is known as electrostatic attraction [80].

1.4.8.3 Hydrogen bonds

These are bonds produced between molecules, which are located between the hydrogen atom and the less electronegative atom Another method is more electronegative, known as using an electron pair[81].

1.4.9 Adsorption application areas

Adsorption is used for multiple purposes including[82]:

- Liquid separation
- Air drying
- Gas separation and purification
- water treatment

1.4.10 Adsorbent material

The significant technological advancements and harmful industrial waste have led to the development of various techniques to address the pollution they cause. Adsorption has played a major role in these treatments. Due to the increasing applications and diversity of these fields[83], there are numerous options for using different types of adsorbents. There are organic and inorganic adsorbents. Many prepared inorganic materials have been used as adsorbents, some of which have been used despite their weakness due to their low cost, while some organic materials have proven to be highly effective adsorbents[84]. Among the organic materials found to be good adsorbents are activated alumina, silica, and zeolites. There are many organic materials used as industrial and natural adsorbents, such as activated carbon and some biopolymers like cellulose, chitin, collagen [85], and others. General specifications are used to express the efficiency of a specific adsorbent material, such as adsorption capacity, selectivity, adsorption rate, cost, compatibility with the adsorption system, and recoverability. Therefore, an adsorbent material is chosen for a specific application based on a set of characteristics that are compatible with the adsorption system. One important and suitable feature of the adsorbent material used in water purification processes is its affordability, and fortunately, titanium phosphate has specifications that distinguish it from others in this process, as it is inexpensive, highly effective, and meets the desired purpose [86].

1.4.11 Advantages of the adsorbent material

A good adsorbent should have the following characteristics:

-It must have high adsorption capacity.

-It should present a fairly larged efined surface.

-It must be available at a low price.

- He must have the ability to find[43].

1.4.12 Physical properties of the adsorbent

All materials have several physical characteristics, such as their ability to absorb and swell in water, their ability for cation exchange, and the presence of a defined porous surface. [74]

1.4.13 Main adsorbents

There are many adsorbents in water pollution control. Among the most common adsorbents: clay, Activated alumina, silica gel, bioadsorbents, activated carbon, zeolite.

■ **clay**: Natural clay minerals have been used by humans since the beginning of civilization. This is because clay materials are considered excellent candidates for use due to their low cost, availability on most continents of the world, and their high ability to mix and exchange ions. Clay materials are characterized by their layered structures and are considered additive materials. These materials are classified based on the differences in their layer structures such as smectite, mica, kaolin, serpentine, pylophyllite, and sepiolite, and these are just some of the different classes of clay. In addition, these materials have special adsorption properties thanks to their large surface area and high porosity [87].

Figure 1.9: Clay as adsorbent

■ **Silica gel**: Silica gel has an amorphous and disordered composition at the microscopic level, allowing it to have a wide distribution of pore size. Due to its polarity, silica gel is considered a water-absorbent material, achieved through physical adsorption, where water is bound to weak van der Waals forces on the surface. The absorbed water remains chemically stable and can be dissolved again[88].

■ **Bioadsorbents**: Biosorption is the process of adsorption of toxic pollutants from aqueous solutions using biological materials called biomaterials. The materials consist of different functional groups that enable them to bond Heavy metal ions, including chitin, chitosan, yeast, fungal biomass, etc. As biological adsorbents or chelating adsorbents [89].

■ **Zeolite**: Zeolite is an adsorbent material characterized by its three-dimensional bone crystalline structure. Thanks to its distinctive structure, zeolite is easily accessible thanks to its open network structure containing cavities and channels that give it adsorbent properties. Zeolite has a high ion exchange capacity, relatively high specific surface areas, and good selectivity. Hence, the use of zeolite has become widely popular as an alternative in fields requiring adsorption applications [87].

■ **Activated carbon**: Activated carbon is among the most common and basic materials for removing sewage contaminants and water purification, removing color and heavy metals, and is an excellent alternative to more expensive treatment methods[45] However, pure porous carbon materials that can be easily penetrated are limited by their insufficient regeneration and adsorption capacity [89].

Figure 1.10: activated carbon

■ **The advantages based on polymers:** Organic polymer-based materials have been found to have applications in pollution control, water purification, and pharmaceutical manufacturing. Both polyacrylic esters and phenolic resins are considered fundamental polymers in this regard [90].

1.4.14 Adsorption models

: phenomena can be described by graphic representations, called isothermal curves. These curves describe the existing relationship, at equilibrium adsorption, between the quantity of dye retained per gram of adsorbent (qe) and the concentration of the same dye in equilibrium solution (Ce) at a given temperature constant [91]. Several models are used and sometimes developed in the literature. We distinguish : Two-parameter models: Freundlich, Langmuir, Temkin, Elovich and Dubinin Radushkevich; Models with more than two parameters: Sips, Tth, Fritz-Schluender, Jossens, Kislev, Redlich-Peterson. [92].

1.4.14.1 Langmuir model

The Langmuir adsorption isotherm was initially developed to describe the adsorption of gases onto solid surfaces. This empirical model assumes that adsorption occurs in a monolayer at specific homogeneous sites on the adsorbent surface. Consequently, the process is often referred to as homogeneous adsorption . The Langmuir isotherm model can be expressed in both linear and nonlinear forms, as shown in equations: 1.1 ,: 1.2 :

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{q_{max}K_L}.\frac{1}{C_e} \tag{1.1}$$

$$q_e = \frac{q_{max}K_LC_e}{1+K_LC_e} \tag{1.2}$$

Where :

q_{max}: The maximum adsorption capacity (mg/g)

K_L: Langmuir constant(l/mg)

C_e:equilibrium concentration of the adsorbate (mg/l)

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

1.4.14.2 Freundlich model

The Freundlich isotherm is one of the earliest models describing non-ideal and reversible adsorption processes. This empirical model is applicable to multilayer adsorption, where there is a non-uniform distribution of adsorption heat and affinities across a heterogeneous surface . The Freundlich isotherm assumes heterogeneous surface energies and is widely used in heterogeneous systems, particularly for highly interactive species or organic compounds on molecular sieves and adsorbents. The Freundlich isotherm model can be expressed in both nonlinear and nonlinear forms, as shown in equations: 1.3 , : 1.4

$$q_e = K_F C_e^{1/n} \tag{1.3}$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{1.4}$$

Where :

q_e:The amount of adsorbed material(mg/g)

C_e:Focus on balance (mg/l)

K_F, n are constants of Freundlich

1.4.14.3 Temkin model

This model relies on the enabling temperature, assuming an increase in the recovery rate of the solid surface, which leads to a linear decrease in the heat of adsorption. It was developed into an enabling equation for the case of gas and solid adsorption and then applied to the liquid phase [40]. The model is expressed by the following nonlinear equation equations: 1.5 :

$$q_e = \frac{RT}{b_T} ln(K_T C_e) \tag{1.5}$$

Where :

q_e: Equilibrium amount adsorbed (mg/g)

C_e:Equilibrium adsorption concentration (mg/l)

R: Gas constant (kj/mol.K)

T: Temperature (k)

b_T and K_T : Characteristic constants of the adsorbent/adsorbate system (j/mol), and (l/mg), respectively.

1.4.15 Adsorption kinetics

Adsorption kinetics are understood through the evolution of the amount of adsorbate and the time required to reach adsorption equilibrium. Adsorption kinetics refer to the rate at which a solute is adsorbed from a solution, providing insights into the adsorption mechanism and the transfer pattern between the liquid and solid phases. This has led to the development of kinetic properties and the application of several models to describe adsorption kinetics and determine the nature of the interactions at the liquid-solid interface [74].

Three types of adsorption kinetics can be distinguished: pseudo-first-order (PFO), pseudo-second-order (PSO), and intraparticle diffusion (IPD).

1.4.15.1 PFO

Typically, the pseudo-first-order kinetic model is used to predict adsorption kinetics. This model assumes that the rate of change of solute uptake over time is directly proportional to the difference between the current solute concentration and the saturation concentration [33]. The rate constant for adsorption is determined using the pseudo-first-order equation, as described by. equations: 1.6 :

$$q_t = q_e(1 - exp^{K_1 t}) \tag{1.6}$$

Where:

q_t: The amount of adsorbate at time t and its unit (mg/g)

q_e: Adsorption capacity at equilibrium per gram of adsorbent (mg/g)

K_1: the rate constant of adsorption (min^-1)

1.4.15.2 PSO

In chemical research involving chemical bonding between metal ions and functional groups, Mackay and Ho proposed in 1999 the second-order pseudo-dynamic reflection, also known as the second-order kinetic model. This model is represented by the following equations: 1.7 :

$$q_t = \frac{q_e^2 K_2 t}{1 + K_2 t} \tag{1.7}$$

Where:

K_2:The rate constant of adsorption for the second-order pseudo-dynamic model (min mg/g)

1.4.15.3 IPD

IPD means Intraparticle diffusion model, the adsorption process is controlled by the diffusion within the particles, which quickly reaches an equilibrium state and continues for long periods for small adsorbates due to the slowdown. The diffusion of particles in these structures has dimensions close to the diameter of the liquid particles[33]. Instead of contact time, the adsorption changes approximately in proportion to $t^{1/2}$, and its equations are of the following form equations: 1.8

$$q_t = K_i t^{1/2} + C \tag{1.8}$$

Where:

The intraparticle diffusion rate constant, K_i (mg/gůmin$^{-1/2}$), can be calculated from the slope of the linear segment of the plot of q_t versus $t^{1/2}$.

1.4.16 Class of isotherm

Classe L :

The L-class isotherm is presented, with weak concentration in solution, a downward-rolling cavity resulting in reduced furcation free sites and measured adsorption evolution. This phenomenon results when the forces of attraction between The adsorbed molecules are invalid. They can be observed when molecules are absorbed horizontally, reducing lateral attraction. Additionally, it may manifest when molecules compete with one another for the opportunity to adsorbed vertically, perhaps resulting in a solvent and solution. The single molecules' absorption in this instance is quite powerful. To minimize adverse effects [46].

∗Classe C :

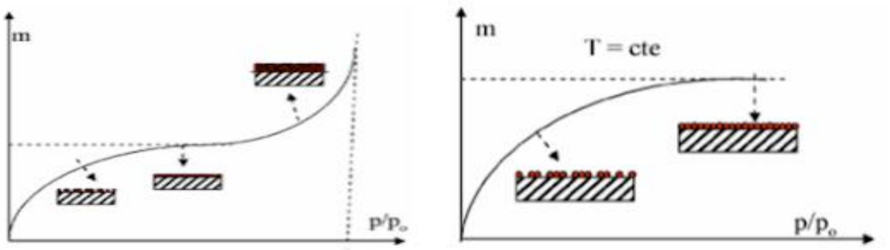
This class of isotherms is characterized by continuous partitioning between the substrate and solution up to the point of pale. Linearity indicates that the number of free sites does not change during the adsorption process. This means that sites are created during the adsorption process. This indicates that isotherms of this class are obtained when solvent molecules are able to change the texture of the substrate by opening pores that were not previously opened by the solvent [46].

∗Classe S :

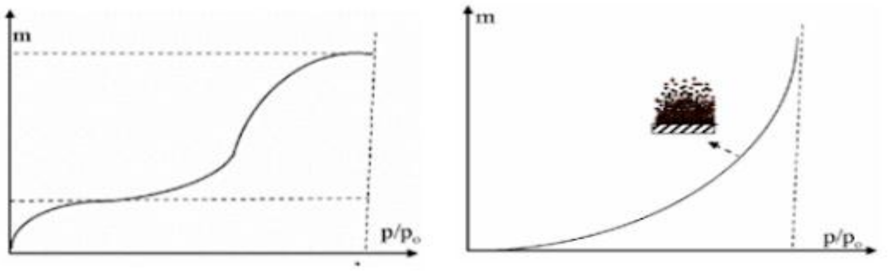
(Collaborative Adsorption). This is due to molecules that are attracted to each other by Van der Waals forces and congregate into clusters where they tase one against the other. This behavior is encouraged in two ways: first, when solvent molecules are adsorbed vertically, as is the case with molecules with a single functional group; and second, when solvent molecules are in strong competition with one another for adsorption [46].

∗Classe H :

The early part of the isotherme is almost vertical, and the amount adsorbable appears to be significant at almost zero concentration of the solvent in the solution. This phenomenon occurs when there are strong contacts between the adsorbate molecules and the solid surface. Additionally, the class H isotherme is observed during the adsorption of micelles or polymers formed from solvent molecules [46].



Isotherms (L) Isotherms (C)



Isotherms (S) Isotherms (H)

Figure 1.11: An image that expresses the four curves of the adsorption isotherm

1.4.17 Thermodynamics of Adsorption

The thermodynamics of the adsorption process are closely related to the temperature of adsorption of metal ions. Exothermic or endothermic adsorption processes can often be used to explain the thermodynamic character of the adsorption of heavy metals on an inexpensive adsorbent. Exothermic adsorption occurs when the rate of adsorption decreases with temperature, while endothermic adsorption occurs when the rate of adsorption increases with increasing temperature. Free energy ΔG°, enthalpy ΔH°, and entropy ΔS° are three thermodynamic parameters frequently used to analyze the behavior of a thermodynamic adsorption system [89]. As shown in the equations: 1.9, 1.10, 1.11.

$$K_d = \frac{q_e}{C_e} \tag{1.9}$$

$$\Delta G^\circ = -RTlnK_d \tag{1.10}$$

$$lnK_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{1.11}$$

where:

ΔG°: Change in free enthalpy (kj/mol).

ΔS°: the change in entropy ($KJ.mol^{-1}.k^{-1}$).

ΔH°: The change in enthalpy (KJ/mol).

R: The ideal gas constant ($8.314 J/mol.k$).

T: Temperature (K).

Physical adsorption is the term commonly used to describe the adsorption process when ΔG° belongs [-20 to 0 (KJ/mol)].

Chemically, the adsorption process takes place when the change in free energy falls between [-80 to -400 (KJ/mol)].

CHAPTER 2

METHODOLOGY

2.1 Introduction

All experiments for this research were conducted in two main laboratories: Laboratory 5, Faculty of Technology, University of El Oued, and Laboratory 105, Faculty of Applied Sciences, Universiti Teknologi MARA (Malaysia).

This chapter comprises three essential parts, summarized as follows:

Preparation of PPP-Raw: This section details the preparation of PPP-Raw, a promising and recoverable adsorbent used to remove pollutants, such as synthetic dyes (MV 2B), from water bodies.

Instruments and Techniques: This part explains the instruments (e.g., SEM, BET, FTIR) and various techniques (e.g., pH pzc) employed in this work.

Optimization of Adsorption Parameters: The third part focuses on determining the optimum adsorption operation parameters using the Box-Behnken design.

2.2 Materials and Chemical Solvent used

Several materials chemicals solvent were used for this work such as sulfuric acid, Sodium hydroxide, and Methyl Violet 2B dye ...etc. The below (Table: 2.1) exhibits: Name, Chemical formula, Properties, and company of industry these materials.

Table 2.1: physico-chemical properties for materials and chemical reagents used.

No	**Name**	**Chemical formula**	**Properties**	**Company**
1	*sulfuric acid*	H_2SO_4	Liquid	Fluka
2	*Sodium hydroxide*	$NaOH$	Liquid	Fluka
3	*Methyl Violet 2B dye*	$C_{24}H_{28}ClN_3$	Powder, MW= 393.94 g/mol, $\lambda_{max} = 575$ nm	Sigma Aldrich
4	*Ultrapure water*	H_2O	Liquid	

2.2.1 Preparation of Prickly Pear Peel Preparation Raw (PPP-Raw)

This study presents a novel approach utilizing prickly pear peels as a natural adsorbent for the removal of MV 2B dye. The initial step involved meticulous rinsing of the prickly pear peels with ultra-pure water to eliminate dust and suspended impurities, followed by a three-day sun-air drying process. Subsequently, the dried peels were ground and sieved to obtain a fine powder. The resulting sample was properly labeled as (PPP-Raw) and stored in sealed jars for future use. The preparation steps for the raw adsorbent of Prickly Pear Peels is presented in Figure 2.1.

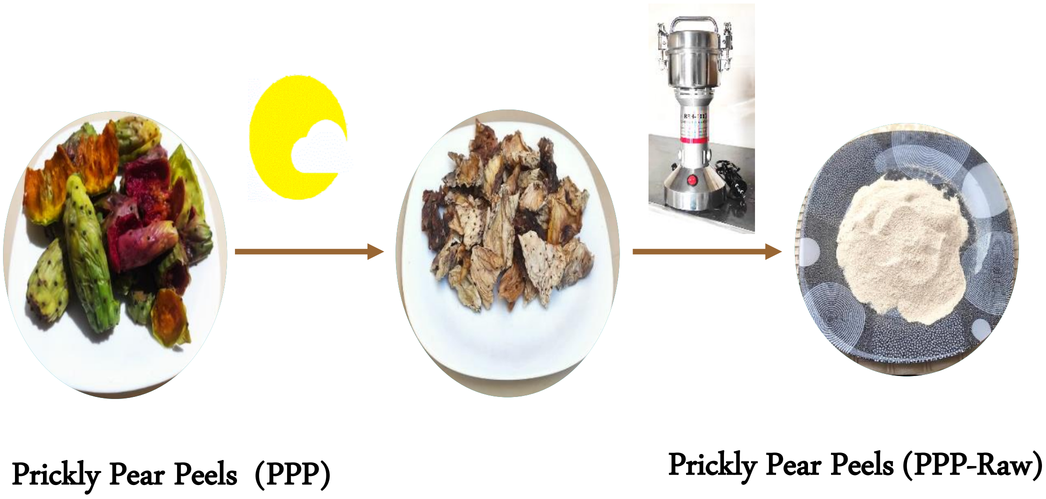


Figure 2.1: Preparation steps for the raw adsorbent of Prickly Pear Peels (PPP-Raw).

2.3 Instrumentation

The prepared sorbent (PPP-Raw) undergoes comprehensive characterization, employing various analytical techniques, including SEM-EDX, FTIR, BET, and pHPZC.Surface morphology analysis is conducted using scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDX) analysis utilizing the Hitachi TM3030Plus Tabletop Microscope from Japan.The functional groups present on the adsorbent surfaces are examined using Fourier Transform Infrared Spectroscopy (FTIR) employing the PerkinElmer Spectrum RX1 instrument. FTIR spectra are recorded across the wave number range of 4004000 cm^{-1} employing the KBr disc method.To evaluate the surface textural properties of the raw sorbent (PPP-Raw), adsorption-desorption isotherms of nitrogen gas are measured at -196 degrees Celsius utilizing the Micromeritics ASAP 2020 analyzer from the USA. Lastly, the pH of the point zero charge of the raw sorbent is determined following the drift method protocol outlined by Babic et al [93].

2.3.1 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) is a highly intriguing method used to capture detailed images of the surface topography of compounds. This technique operates by directing a beam of electrons onto samples that have been coated with gold using a Polaron SC 515 sputter coater, rendering them electrically conductive. The interaction between the electrons and the sample generates various signals, which are processed to create images. It is important to mention that the samples were analyzed using a scanning electron microscope equipped with an energy dispersive X-ray analyzer (SEM-EDX, Hitachi, TM3030Plus, Tabletop Microscope, Japan).

2.3.2 Fourier Transform Infrared Spectroscopy (FTIR)

The fundamental functional groups of the samples were identified using a Perkin-Elmer Spectrum RX I FTIR spectrometer. To prepare the samples, a thin and transparent pellet was created by mixing the sample with potassium bromide, followed by milling and compressing with a mortar and pestle and a hydraulic press, respectively. The pellet was then placed in the cell holder and analyzed with the FTIR spectrophotometer. All spectra were recorded over a wavenumber range of 4000-450 cm^{-1}.

2.3.3 Brunauer-Emmett-Teller (BET)

The surface area, total pore volume, and mean pore diameter of the samples were estimated using Brunauer-Emmett-Teller (BET) analysis. These characteristics were measured with a Micromeritics surface area analyzer (Model ASAP 2020, USA). The results provided the surface area in (m^2/g),total pore volume in cmş/g, and mean pore diameter in nm.

2.3.4 Zero Point of Charge (pH pzc)

The Jeon and Holl technique (Dalvand et al., 2016) is one of the methods used to determine the surface charge of samples (positive, negative, or zero). The procedure involves taking 100 mL of a 0.01N NaCl solution into a series of conical flasks, with the pH adjusted to values ranging from 2 to 12 using 0.01N HCl or 0.01N NaOH. The initial pH values were measured with a Metrohm 827 pH lab meter. Next, 100 mg of each adsorbent was added to these solutions, and the mixtures were agitated for 24 hours at 100 rpm in a shaker bath incubator. The final pH was then recorded, and a graph of final pH versus initial pH was plotted. The point of zero charge (pHpzc) was determined as the intersection of the curve with theorizontal line representing pH.

2.3.5 Design of experiments

To assess the influence of different environmental conditions, notably PPP-Raw dose, pH, and reaction time, on the adsorption performance of MV 2B, a Box-Behnken design with response surface methodology (BBD-RSM) was adopted (as outlined in Table 2.2) featuring a second-order quadratic polynomial equation (refer equation 2.1). The experimental arrangement involved the addition of three different quantities (0.02 g, 0.06 g, and 0.1 g) of PPP-Raw to an MV 2B dye solution with a concentration of 100 mg/L in an aqueous medium (ranging from 20 mg/L to 300 mg/L) as detailed in Table 2.3. The melange was shaken at 100 rpm for 90 min.A total of 17 experimental trials were meticulously duplicated to ensure the reliability of the data extracted in this study.

$$Y = \beta_0 + \sum_{j=1}^{m} \beta_j x_j + \sum_{j=1}^{m} \beta_{jj} x_j^2 + \sum \sum_{i<j=2}^{m} \beta_{ij} x_i x_j + \epsilon \tag{2.1}$$

Herein, β_0 is a constant coefficient, while x_i and x_j denote the factors being studied (i and j vary from 1 to m). The coefficients β_j, β_{jj}, and β_{ij} represent the linear, binomial, and combined effects, respectively. The value of m represents the total number of factors being studied, and ϵ indicates the error term

The experiments data of the optimization process as well as the MV 2B removal as a response are recorded in (Tables: 2.2 , 2.3). A specific amount of the studied adsorbent was added to a 250 mL Erlenmeyer flask containing 100 mL of MV 2B solution (100 mg/L). The mixture was then subjected to shaking using a thermostat water bath shaker. The change in the MV 2B concentrations was followed using HACH DR 3900 spectrophotometer at λ max 575 nm.

Table 2.2: Codes and actual variables and their levels in BBD

		Levels		
Factor code	**Variable name**	**Lowest (-1)**	**Centre (0)**	**Highest (+1)**
A	PPP-Raw dose (g)	0.02	0.06	0.1
B	pH	4	7	10
C	reaction time (min)	10	50	90

Table 2.3: The 3-variables BBD matrix and experimental data for MV 2B dye removal.

Run	**A: PPP-Raw dose**	**B: pH**	**C: reaction time**	**MV 2B removal (%)**
1	0.02	4	50	60.96
2	0.1	4	50	79.16
3	0.02	10	50	78.29
4	0.1	10	50	89.17
5	0.02	7	10	64.56
6	0.1	7	10	79.77
7	0.02	7	90	75.2
8	0.1	7	90	83.96
9	0.06	4	10	71.05
10	0.06	10	10	85.05

11	0.06	4	90	78.37
12	0.06	10	90	89.45
13	0.06	7	50	82.99
14	0.06	7	50	85.03
15	0.06	7	50	83.5
16	0.06	7	50	83.6
17	0.02	7	50	84.82

2.3.6 Batch adsorption study

Experiment 12 results from Table 2 conclusively demonstrate that the most effective removal of dye from aqueous solutions is attained under specific experimental conditions: PPP-Raw dose (A) of 0.06 g in 100 mL, pH maintained around 10 (B), and a reaction time (C) of 90 min. Consequently, these optimized experimental parameters were adopted for the batch adsorption study.

Kinetic adsorption experiments were executed utilizing 100 mL of a 100 mg/L MV 2B solution with 0.1 g of PPP-Raw sorbent, meticulously sampled at specified time intervals (10, 15, 30, 60, 120, 180, and 240 min). Meanwhile, isotherm and thermodynamic experiments were carried out under identical conditions, utilizing MV 2B solutions ranging from 20 to 300 mg/L and conducted at temperatures of 25, 35, 45, and 55 , respectively. Subsequently, the dye-adsorbent mixture underwent filtration through a 0.45 μ needle filter (organic system). The absorption values of the separated MV 2B dye solutions were determined using a UVVis spectrophotometer (HACH DR 3900 / Germany) set to a wavelength of 575 nm. The percentage of color removal (CR; %) of MV 2B was calculated using the following formula:

$$CR\% = \frac{\text{the initial concentration (mg/L)} - \text{the equilibrium concentration (mg/L)}}{\text{the initial concentration (mg/L)}} \times 100 \tag{2.2}$$

CONCLUSION

In conclusion, the raw prickly pear peel as an eco-friendly and cost-free method was successfully used for the removal of MV 2B dye. The RSM-BBD results indicated that PPP-Raw exhibits a relatively high adsorption capacity, achieving 89.45% removal efficiency with two significant interactions, AB(p-value= 0.0120), and AC(p-value= 0.0209). The physicochemical analysis revealed that the surface of PPP-Raw contains OH, NH, and COOH functional groups. These nucleophilic groups, in an alkaline medium, enhance the adsorption capacity of PPP-Raw for MV 2B dye through electrostatic attraction, hydrogen bonding, and $\pi - \pi$ interactions.In addition, the adsorption experiments demonstrated that PPP-Raw can withstand various environmental conditions, recording a maximum adsorption capacity (qmax) of 569.6 mg/g. Thus, the adsorption of waste dye pollutants using PPP-Raw is feasible and holds significant potential for industrial applications.

Future Recommendations

Based on the results of this study, the following recommendations should be considered for future work:

- Promoting the utilization of agricultural waste to preserve the environment.
- response surface methodology is considered very important to optimize adsorption process factors.
- Utilize this adsorbent for the removal of heavy metals in wastewater treatment.

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