REPUBLIQUE ALGERIENNE DEMOCRATIQUE ET POPULAIRE

MINISTERE DE L'ENSEIGNEMENT SUPÉRIEUR ET DE LA RECHERCHE SCIENTIFIQUE

UNIVERSITÉ 20 AOÛT 1955 SKIKDA

FACULTE DE TECHNOLOGIE

DÉPARTEMENT DE GÉNIE DES PROCÉDÉS

Mémoire

En vue de l'obtention du diplôme de

Master

Filière : Génie des procédés

Spécialité : Ingénierie & Gestion de l'Eau

Application of Response Surface Methodology (RSM) for Crystal violet dye removal from aqueous solution using modified adsorbents

Soutenu le 24/06/2023

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Année Universitaire 2022- 2023

Dedication

All forms of the most beautiful praise, and in all

circumstances are to Allah alone.

I dedicate this work to all those who are dear to my heart:

I dedicate this modest work to the one who gave me life, the symbol of tenderness,

who sacrificed himself for my happiness and success,

to my Mother

To my father who was for me a school in life in himself

To my dear brothers, Mouloud

Tarek

Abd Errezak

And our little Seif Allah

To all the members of my great Mammeri and Kaddeche family, near and far.

To all my colleagues over the years

To the most important friends that life has introduced me to

To all those who have helped me from afar in my formation.

Finally, I thank my buddies Khane Abderrezak and Bougouizi Lamine who are

Contributes to the realization of this modest work.

Mammeri Mohammed

Lakhdar

Abstract

In this study, biomass wastes were used as alternative precursors for producing high surface area biosorbent (referred to as MM1 and MM2) using chimical activation. The adsorption characteristics of modified biosorbent 1 and modified biosorbent 2 were studied by investigating the removal of a model cationic dye (crystal violet, CV). To optimize important adsorption variables (initial CV concentration, pH, temperature and biosorbent dose), the numerical desirability function of the Box-Behnken Design (BBD) and Central Composite Design (CCD) were used. The numerical desirability function of the Box-Behnken Design and Central Composite Design were used to optimize important adsorption variables (A: initial CV concentration (5–100 mg/L) ; B : pH (2-10) ; C : temperture (20-60) and D: biosorbent dose (0.025-0.2 g).

Keywords: Biomass wastes, Adsorption, Crystal violet dye, Response surface methodology, Box-Behnken Design, Central Composite Design.

Résumé

Dans cette étude, les déchets de biomasse ont été utilisés comme précurseurs alternatifs pour la production de biosorbant à grande surface (appelé MM1 et MM2) en utilisant l'activation chimique. Les caractéristiques d'adsorption du biosorbant modifié 1 et du biosorbant modifié 2 ont été étudiées en étudiant l'élimination d'un colorant cationique modèle (cristal violet, CV). Pour optimiser d'importantes variables d'adsorption (concentration CV initiale, pH, température et dose de biosorbant), la fonction de désirabilité numérique du plan Box-Behnken (BBD) et du plan composite central (CCD) a été utilisée. La fonction de désirabilité numérique du plan Box-Behnken et du plan composite central a été utilisée pour optimiser d'importantes variables d'adsorption (A : concentration CV initiale (5–100 mg/L) ; B : pH (2-10) ; C : température (20-60) et D : dose de biosorbant (0,025-0,2 g).

Mots-clés : Déchets de biomasse, Adsorption, Colorant violet cristallin, Méthodologie de surface de réponse, Box-Behnken Design, Central Composite Design.

ملخص

في هذه الدراسة ، تم استخدام نفايات الكتلة الحيوية كسلائف بديلة لإنتاج الممتز الحيوي عالي المساحة (المشار اليه باسم MM1 و MM2) باستخدام التنشيط الكيميائي. تمت دراسة خصائص الامتزاز للممتز الحيوي المعدل 1 والممتز الحيوي المعدل 2 من خلال التحقيق في إزالة الصبغة الكاتيونية النموذجية (الكريستالي البنفسجي CV). لتحسين متغيرات الامتزاز المهمة (تركيز الكرسالي البنفسجي الأولي ، ودرجة الحموضة ، ودرجة الحرارة ، وجرعة الممتز الحيوي) تم استخدام دالة الرغبة العددية (BBD) و التصميم المركب المركزي (CCD). حيث تم استخدام دالة الرغبة العددية لتصميم -Box إضافة Behnken إضافة الى التصميم المركب المركزي من اجل تحسين متغيرات الامتزاز المهمة (أ: تركيز الكريستالي البنفسجي الأولي (100-5 ملغ/ل) ؛ ب: درجة الحموضة (10-2) ؛ ج: درجة الحرارة (60-20) ؛ د: جرعة الممتز (0.2-0.025 غ).

الكلمات المفتاحية: نفايات الكتلة الحيوية، الامتزاز، صبغة الكرستالي البنفسجي، منهجية سطح الاستجابة، تصميم المركب المركزي، تصميم Box-Behnken.

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GENERAL INTRODUCTION

Everyone agrees today that our planet is going wrong. Indeed, effluents of industrial, agricultural and domestic origin generate a wide variety of chemicals that flow into rivers, seas, groundwater and lakes, jeopardizing (threatening) the fragile natural balance that has allowed life to develop on earth. The problem is even more serious in the case of industrial effluents, which are much more toxic. Water pollution by minerals and organics is a source of environmental degradation and is currently of particular international interest. The importance attached to the protection of natural environments and the improvement of water quality continues to grow **[1].**

The sudden and massive release of toxic residues into the natural environment such as textile dyes has led to the appearance of many risks for the balance of the natural environment and ecosystems, but also for man himself, the producer of this waste and instigator of this great imbalance. This has therefore stimulated man to preserve the quality of natural environments and in particular surface and groundwater. The majority of purified water is currently discharged. The generalization of the reuse of this water can therefore contribute to partially filling the water deficit **[2].**

Primary industries responsible for the discharge of coloring compounds in aquatic ecosystems are textile industries (54 %) accounts half of the existing dye effluents present in the worldwide environment followed by the dyeing industries (21 %), paper and pulp industries (10 %), tannery and paint industries (8 %), and the dye production industries (7 %) **[3].** Dyes discharged by industries into water bodies are not degradable, so different methods are used for their removal from water **[4].** Various methods such as coagulation, sedimentation, precipitation, filtration, flocculation, ion exchange, membrane- based processes, photo catalysis, oxidation, adsorption, and advanced processes such as chlorination, ozonation, nanotechnology, and microorganisms such as algae, fungi and bacteria are used for the removal of dyes from wastewater. These methods have their own advantages and disadvantages. Among these methods we choose adsorption for its low-cost procedure and its easily available adsorbents **[5].**

Crystal violet (CV) dye is triphenylmethane cationic dye. It is used in textile and paper dye industries as well as navy blue and black inks for printing, ball-point pens and inkjet printers. It is also used to colourize diverse products such as fertilizers, antifreeze, detergents and leather. Crystal violet is also used as a histological stain, particularly in Gram staining for classifying bacteria **[6,7].** Disposal of dyes in wastewater is a source of water contamination and disturbance of aquatic life **[8].** Therefore, a suitable and efficient method is critically required to treat the wastewater containing dyes such as Crystal violet **[9,10].**

Response surface methodology (RSM) is basically a collection of mathematical and statistical methods that is useful for designing the experiments, developing models by considering the interactions of parameters, and process optimization **[11-13].** RSM is based on fitting the mathematical models (linear, square polynomial functions and others) to the experimental results from the designed set of experiments and verification of the model obtained by the statistical techniques **[14].**

The purpose of the present study was to examine and optimize the effect of initial dye concentration, pH, temperature and adsorbent dose on dye adsorption Central Composite Design (CCD) and Box-Behnken Design (BBD).

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Chapter I: Dyes and environment

Chapter I: Dyes and environment

I.1. Introduction

Dyes are widely used for industrial, printing, food, cosmetic and clinical purposes as well as textile dyeing because of their chemical stability, ease of synthesis, and versatility. Their stability, however, causes pollution once the dyes are released into the environment in effluents **[1].**

The residual dyes from different sources (e.g., textile industries, paper and pulp industries, dye and dye intermediates industries, pharmaceutical industries, tannery, and Kraft bleaching industries, etc.) are considered a wide variety of organic pollutants introduced into the natural water resources or wastewater treatment systems **[2].**

Dyes are organic-coloured compounds imparting the colour to substrates like hair, drugs, paints, paper, wax etc. These are coloured because absorbs visible light at certain wavelength. All coloured compounds are not dyes but dyes are coloured **[3].**

I.2. Usage history of organic dyes

Colour, which contributes so much to the beauty of Nature, is essential to the attractiveness and acceptability of most products used by modern society **[4].** As long ago as the 25th century BC man coloured his surroundings and clothes using a limited range of natural colorants of both animal and vegetable origin. Alizarin extracted as the glycoside rubierythric acid from madder, was used by the ancient Egyptians and Persians, the use of indigo obtained from Indigofera dates back to 3000 BC, and Tyrian Purple, prepared from the sea snail Murex brandaris, has been used since the Roman era. However, that was until the mid-nineteenth century at the British empire, where the teenager student William Henry Perkin under the care of his mentor the celebrated German chemist August Wilhelm von Hofmann was trying to find a mor affordable way to obtain quinine, which was a natural substance expensive to obtain since it was extracted from the bark of the cinchona tree, which only grew in the tropical forests of the Andes (South America). And that was for the cause of stopping the infection of malaria among the Brittan soldiers. Until he **accidentally discovered the first synthetic organic dye in history in 1856**, that of the colour mauve which is called by many names now (aniline purple, mauveine, purple aniline or Perkin's mallow). It was a profitable mistake that demonstrated the enormous possibilities of chemistry, a science that in the mid-nineteenth century had just been born and scarcely had any applications, but over time we observe how this discovery changed the history of chemistry and gave birth to the development of many other important sectors of the modern chemical industry **[5,6].**

I.3. Organics dyes Definition

Organic colours are derived from plants and animals and form soluble dyes which can bond with a substrate such as fabric, paper or leather. In order to be used as a pigment, dyes must be precipitated onto an inert substrate such as alum to form what is called a lake **[7].**

I.4. Types of organic dyes

Organic dyes are basically classified into two types:

I.4.1. Natural

Naturel dyes are obtained from plants like leaves, root, bark etc. and animals for example: Alizarine (obtained from Madder plant), Blue dye (Indigo), Red dye or Carmine red (Carmic acid) obtained from coccus cacti, cochineal (obtained from Insect). Natural dyes are few in numbers and have limited shades/colours **[3].**

I.4.2. Synthetic

The raw materials for synthetic dyes are compounds such as benzene, derived from the distillation of coal. It is for this reason that synthetic dyes are commonly referred to as coal tar dyes. From these raw materials, the intermediates are made by a series of chemical processes which, in general, correspond to the replacement of one or more hydrogen atoms of the starting material by particular elements or radicals.

I.5. Classification of organic dyes

Dyes can be classified according to their mode of application on substrates or their chemical structure.

I.5.1. Mode of application on substrates

This classification is based on the various methods of dyeing different fibres with dyes.

I.5.1.1. Direct or substantive dyes (soluble in water)

These dyes applied directly to the fabrics in aqueous solution. It consists of soaking the fabric in an aqueous solution of the dye, taking it out, removing excess of the solution and then drying. Direct dyes are strongly polar dyes used to dye polar fabrics (e.g., wool) or moderately polar fabrics (e.g., cotton, rayon). The dyeing of the fibres is carried out in the presence of common salt, so these dyes are also called salt dyes such as Congo red.

These dyes are further subdivided into two groups:

a) Acidic dyes

Nitronaphthols (e.g., martius yellow, picric acid, Naphthol yellow-S), acid orange-7 (orange-II) are acidic dyes. These dye, wool and silk (proteinous in nature) directly due to interaction of the polar acidic group of the dye with the basic ($-NH_2$) group of the fibre.

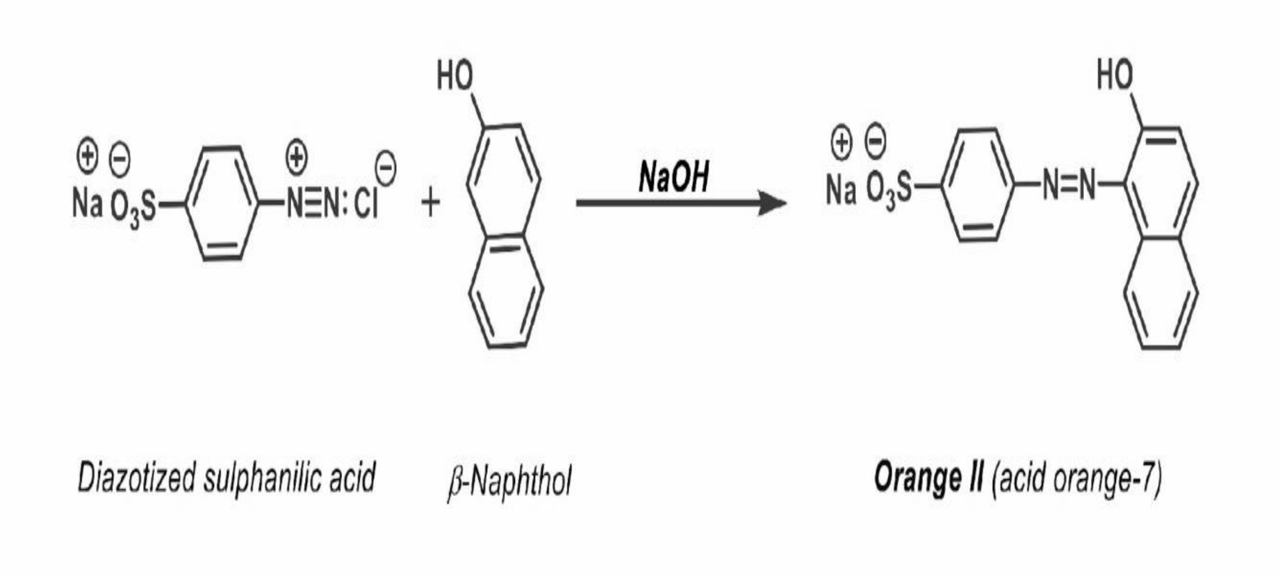

Fig. I.1. Chemical structure of an acidic dye.

b) Basic dyes

These are the cationic dyes containing basic groups such as $–NH_2$, –NHR, $–NR_2$ and their salts (mostly in the form of HCl and $ZnCl_2$ salts). These are used for dyeinganimal fibres directly but cotton (vegetable fibres) after moderating with tannin. For example, Malachite green, Magenta, para-rosaniline, etc.

In recent years, azo dyes with $–NH_2$ group, like aniline yellow and butter yellow are also considered as basic dyes due to their basic nature.

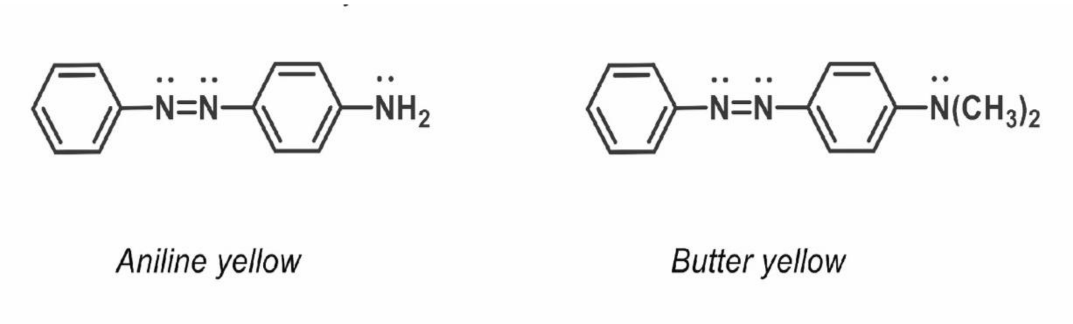

Fig. I. 2. Chemical structure of a basic dye.

I.5.1.2 Vat dyes (insoluble in water)

These dyes applied directly on the fibre. These can be used only on cotton & rayon and not on silk & wool. The dyeing, in this case, is a continuous process and is carried out in a large vessel called vat. For this reason, these dyes are termed as vat dyes.

For example, Indigo blue, Tyrian purple (6,6-dibromoindigo).

These dyes are insoluble in water and first of all converted into water soluble form (leuco compound) by reduction (referred to as vatting) in alkaline medium which may be colorless. It is in this form they are introduced into the fabric. The fabric is then dried in air where oxidation takes place and colored fabric is obtained.

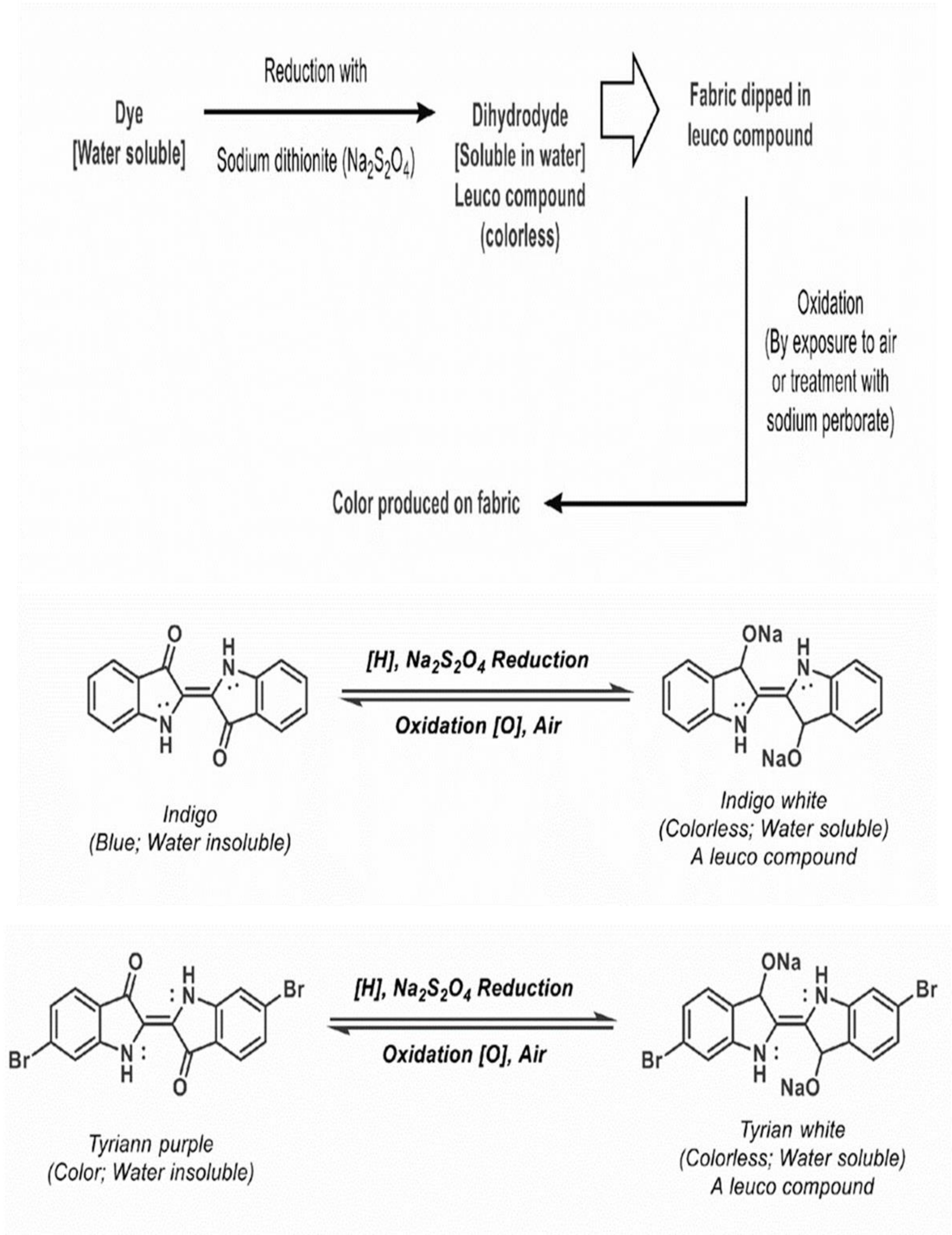

Fig. I. 3. Chemical structure of some vat dyes.

I.5.1.3 Mordant dyes (or indirect or adjective dyes) (insoluble in water)

These dyes are insoluble in water and a third substance is used as a binding material of the fibre with dye. This third substance is called mordant and such dyes are called mordant dyes.

In the dyeing process, fibre is dipped in mordant, dried and then again dipped into the dye solution. Mordant forms a complex with the dye and is deposited on the fibre giving it a permanent shade.

For acid dyes, a basic mordant [like metal salts $Fe(OH)_3$, $Al(OH)_3$] is used and for basic dyes, an acid mordant such as tannic acid is used. Alizarin is an example of mordant dyes. It gives different colors when used with different materials. It gives a red color with Al and Sn salts, brownish red tones with Cr mordant, and black-violets with Fe mordant.

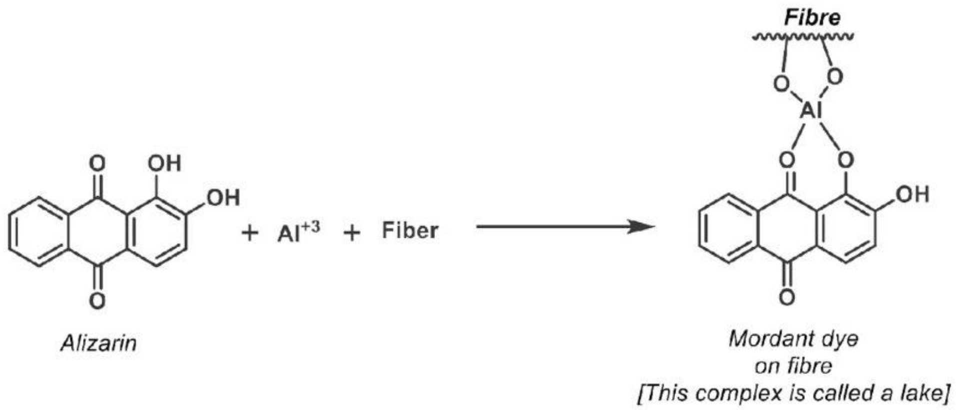

Fig. I.4. Chemical structure of a mordant dye.

I.5.1.4 Disperse dyes (insoluble in water)

These dyes are insoluble in water, but are capable of dissolving certain synthetic fibres. Disperse dyes are usually applied in the form of a dispersion of finely divided dye in a soap solution in the presence of some solubilizing agent such as phenol, cresol, or benzoic acid etc. The absorption into the fibre is carried out at high temperatures and pressures. Disperse dyes are used to dye acetate rayons, Dacron, Nylon and other synthetic fibres.

For example: Celliton Fast Pink B (1-amino-4-hydroxyanthraquinone) and Celliton Fast Blue B (1,4-N,N'-dimethylaminoanthraquinone).

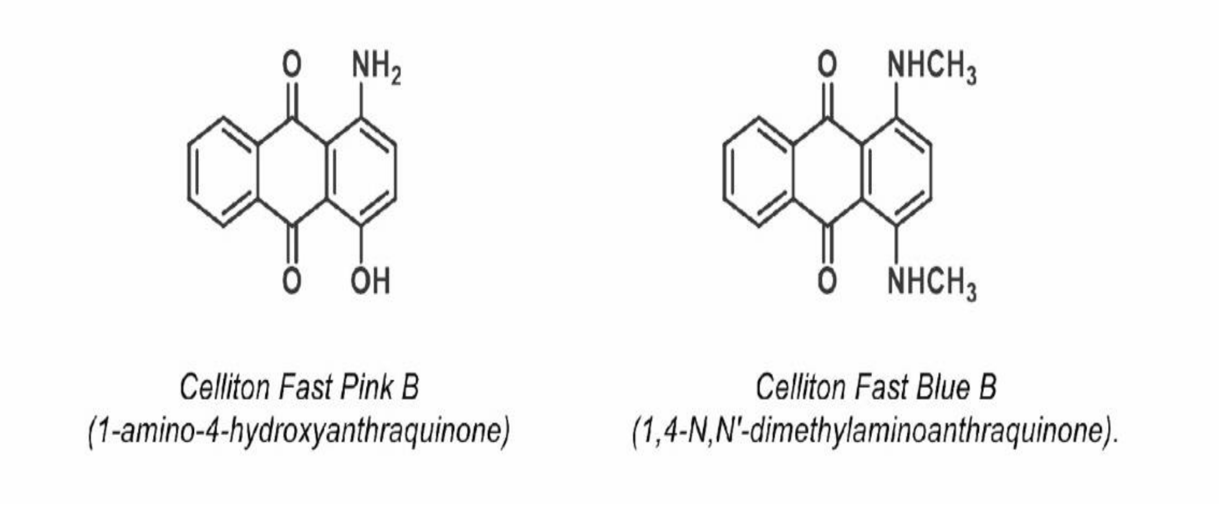

Fig. I. 5. Chemical structure of some disperse dyes.

I.5.1.5 Sulfur dyes (insoluble in water)

These dyes are soluble in sodium sulfide (Na_2S) solution and thus the dyeing process is carried out in Na2S solution. These dyes are generally used for dyeing cotton fibre.

I.5.2. Chemical structure of dyes

According to this, dyes can be classified into following types: The second classification is based on the nature of the group of atoms responsible for the coloring of the compound, that is to say on the nature of the chromophore. The most important dyes are azo dyes, such as Congo red. These dyes represent about 50 p. 100 of the world production of coloring substances and they have a very wide field of application. Other important dyes are triphenylmethane dyes, such as magenta and methyl violet, phthalein dyes, azine dyes, such as mauve, and anthraquinone dyes, such as alizarin. An important new family of dyes are the phthalocyanines, which are blue or green in color and have a chemical structure similar to that of chlorophyll.

A stain is a chemical dye or pigment used to color glass, paper, textiles or wood. Its formulation is based on alcohol, oil or water. A stain is transparent and less thick than a paint or coating, and it penetrates the structure of the material on which it is applied. In research, a dye can be used to make small transparent structures appear by microscopy. The textile industry represents 70 % of the total use of dyes. The classification principles most commonly encountered in the textile industries, are based on the chemical structures of synthetic dyes **[9].**

I.5.2.1. Anthraquinone dyes

Are the most important after azo dyes. Their general formula derived from anthracene shows that the chromophore is a quinone nucleus on which can attach hydroxyl groups to the amino.

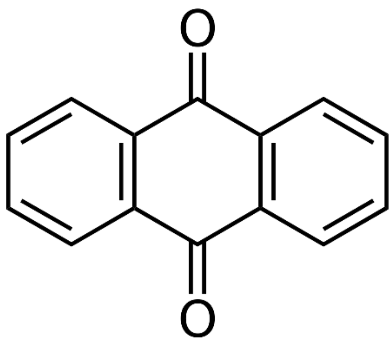

Fig.I.6. structure of an anthraquinone dye.

I.5.2.2. Indigoid dyes

Take their name from the indigo from which they derive. Thus, the selenium, sulfur and oxygen counterparts of indigo blue cause significant hypochromic effects with colors that can range from orange to turquoise.

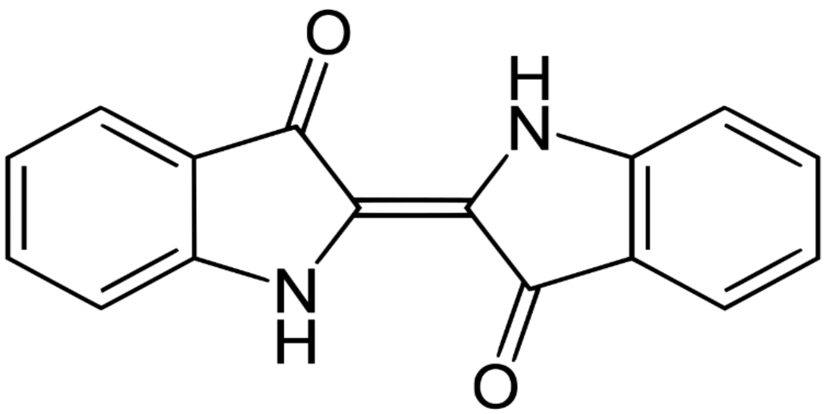

Fig. I. 7. Structure of an indigoid dye.

I.5.2.3. Xanthene dyes

Whose best-known compound is fluorescein, are endowed with an intense fluorescence little used as a dye, their ability as markers during maritime accidents or as flow tractors for underground rivers is despite everything well established.

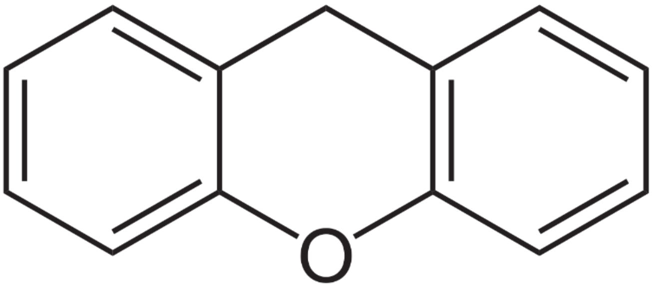

Fig. I. 8. Structure of a xanthene dye.

I.5. 2.4. Azo dyes

These are applied directly on the fiber. The process includes the diazotization and the coupling reaction at low temperature on the fiber itself. The fabric is soaked in an alkaline solution of phenol followed by drying and then immersed in a cold solution of a diazonium salt. The azo dye is developed directly on the fiber itself. Such dyes, known as developed dyes, are called Ice colors also because such dyes formed at low temperature within the fabric.

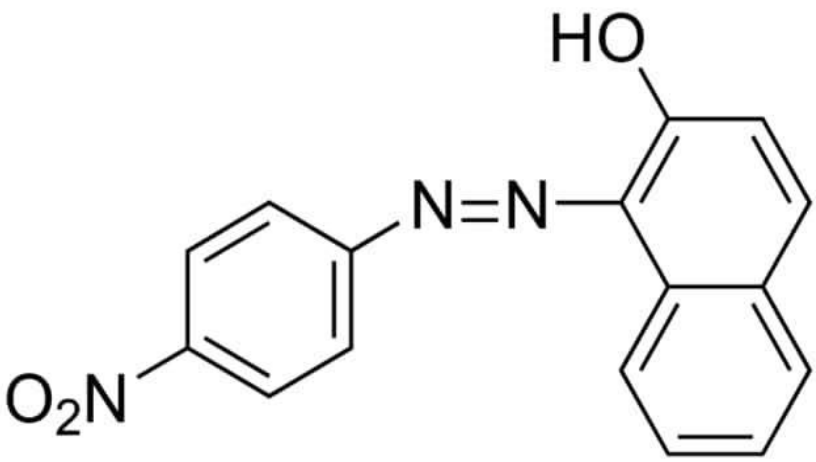

Fig. I. 9. Structure of an azo dye.

I.5.2.5. Nitrite and nitroso dyes

Form a class of dyes very limited in number and relatively old. They are currently still used, because of their very moderate price linked to the simplicity of their molecular structure characterized by the presence of a nitro group (NO_2) in the ortho position of an electron-donating group (hydroxyl or amino groups) **[10].**

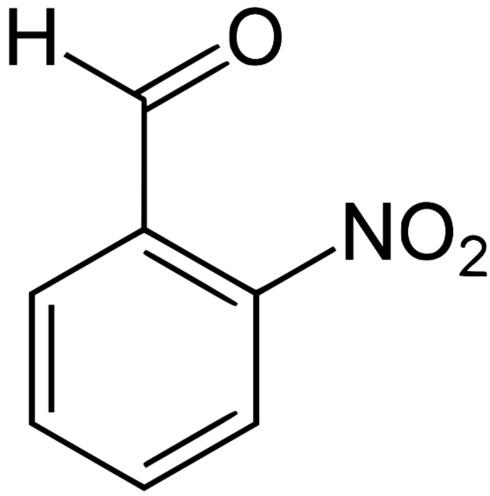

Fig. I.10. Structure of a nitroso dye.

I.6. Areas for using organic dyes

These substances have a very broad spectrum of use. Their main areas of application cations are in particular: the colouring of paper, leather, plastics, varnishes, paint, inks, cosmetics, food and pharmaceutical products. In photography as sensitizers, in Biology for staining microscopic preparations as well as colour indicators in chemistry. In order to understand the importance of dyes, it suffices to examine the percentage of presence of these chemical species, in manufactured products, for the various fields of application **[8].**

- Textiles 60%
- Papers 10%
- Plastics and elastomers 10%
- Leather and furs 3%
- Other applications relate to food products, wood, photography 17%.

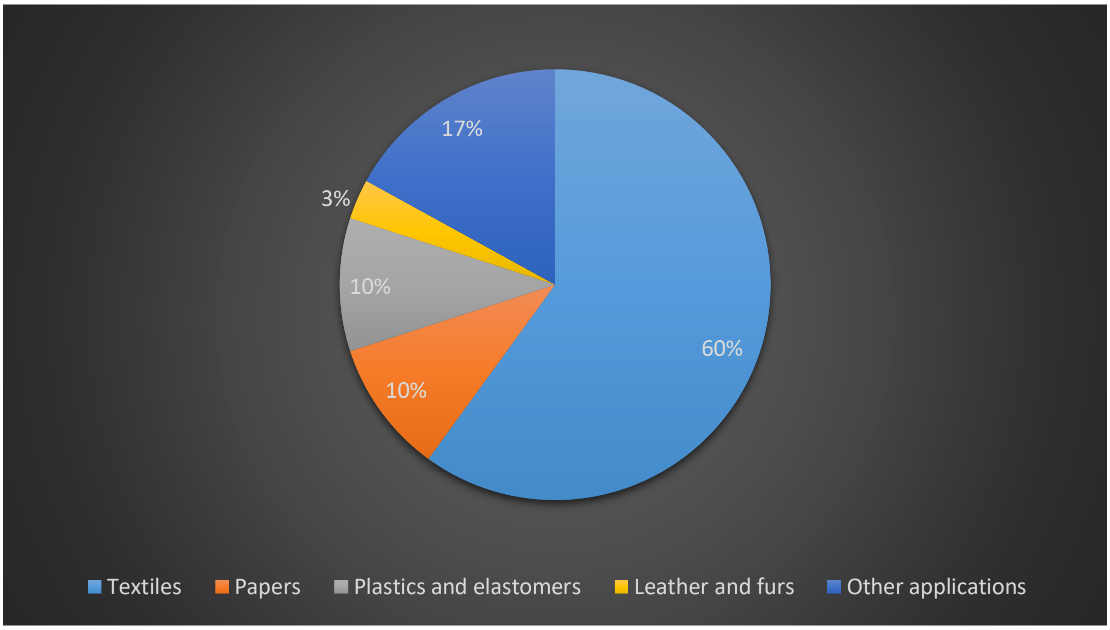

Fig. I.11. Relative circle showing the percentage of some chemical species for various fields of application.

I.7. Environmental impacts

I.7.1. Eutrophication

Under the action of microorganisms, dyes release nitrates and phosphates into the natural environment. These mineral ions introduced in excessive quantities can become toxic for fish life and alter the production of drinking water. Their consumption by aquatic plants accelerates their anarchic proliferation and leads to oxygen depletion by inhibition of photosynthesis in the deepest strata of stagnant watercourses.

I.7.2. oxygenation

When significant loads of organic matter are added to the environment via occasional releases, the natural regulatory processes can no longer compensate for bacterial oxygen consumption. The degradation of 7 to 8 mg of organic matter by micro-organisms is enough to consume the oxygen contained in one liter of water **[11].**

I.7.3. Color, turbidity, odor

The accumulation of organic matter in waterways leads to the appearance of bad tastes, bacterial proliferation, pestilential odors and abnormal coloring. A coloration could be perceived by the human eye from 5.10 66 g per litre. Apart from the unsightly appearance, coloring agents have the ability to interfere with the transmission of light in water, thereby blocking the photosynthesis of aquatic plants **[12].**

I.7.4. Long term hazards

I.7.4.1. Persistence

Synthetic organic dyes are compounds that cannot be purified by natural biological degradation **[13].** This persistence is closely related to their chemical reactivity:

unsaturated compounds are less persistent than saturated ones. alkanes are less persistent than aromatics.

The persistence of aromatics increases with the number of substitutes, halogen substitutions increase the persistence of dyes more than the alkyl group.

I.7.4.2. Bioaccumulation

If an organism does not have specific mechanisms either to prevent resorption once it is absorbed, then this substance accumulates. Species at the upper end of the food chain, including humans, find themselves exposed to levels of toxic substances that can be up to a thousand times higher than the initial concentrations in the water.

I.7.4.3. Cancer

While most dyes are not directly toxic, a significant portion of their metabolites is. derivative for triphenylmethanes **[14].**

I.8. Conclusion

Compared with natural dyestuffs, synthetic colorants are better able to meet the increasingly rigorous technical demands of the present day in terms of stability, fastness, etc. Colour can add not only aesthetic appeal, but frequently provides an almost irreplaceable safety feature (traffic lights and signs, drug identification, control systems).

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Chapter II: Methods of organic dyes removal

CHAPTER II: METHODS OF ORGANIC DYES REMOVAL

II.1 Introduction

Several processes have been used for the treatment of water polluted by refractory organic compounds, toxic and non-biodegradable, from industrial activities which, depending on the type or types of manufacture, generate continuous or discontinuous pollutant discharges of extreme diversity.

Which leads us to point out the intense and irrational use of dyes and the enormous risk to environmental quality and human health that has led to several efforts to eliminate these pollutants. Biological, physical and chemical processes have been developed to eradicate these dyes from aquatic environments **[1].**

II.2 Physical processes

II.2.1. Adsorption

It is a process which consists in transferring the pollutant from its original environment or the fluid phase (liquid or gaseous) towards the surface of the adsorbent (solid). This method of treatment remains, despite everything, very limited for the elimination of all the dyes. Only cationic dyes, mordant dyes, disperse, reactive and vat dyes are removed by this technique, even when using activated carbon, considered the most effective adsorbent. To describe the mechanisms of this phenomenon, several theoretical models have been developed **[2].**

II.2.2. Membrane filtration

In this process, pollutants are retained by a semi-permeable membrane whose the diameter of the pores is less than that of the molecules to be eliminated. This technique is widely used in seawater desalination **[3].**

II.3. Processes physio-chemical (coagulation - flocculation)

Under the term coagulation - flocculation, we mean all processes physicochemical by which colloidal particles or solids in fine suspension are transformed by chemical flocculants into more visible and separable species (flocs). The flocs formed are then separated by settling and filtration and then evacuated **[4].**

II.4. Chemical processes

Chemical oxidation techniques are generally applied for the treatment of hazardous organic compounds present in low concentrations, in pre-treatment before biological processes to reduce the pollutant load, the treatment of wastewater loaded with constituents resistant to biodegradation methods, in post-treatment to reduce aquatic toxicity **[5].**

II.5. Biological processes

Based on microorganisms in aerobic (presence of oxygen) or anaerobic environments (absence of oxygen), biological treatment is a method that may be necessary for the degradation of synthetic organic compounds such as dyes. This process can lead either to total biodegradation with the formation of CO_2 and H_2O, or to incomplete biodegradation, which can result in a compound with a different structure from the parent produced. However, synthetic dyes used in textiles have been shown to be resistant to biodegradation **[6].**

II.6. Some advanced methods for removing organic dyes

II.6.1. Advanced Oxidation Process

Advanced oxidation method is one of the traditional methods that have been applied for de-colorization process. It is based on the mechanism involving generation of

hydroxyl radicals (as oxidizing agents), that when attack upon chromo-genic groups, leads to produce organic per-oxide radicals and ultimately transform them into CO_2, H_20 and inorganic salts. It consists of a variety of methods such as ozonation, use of hydrogen peroxide and Fenton's process that has been discussed here **[7].**

II.6.2. Using Hydrogen Peroxide

Hydrogen peroxide has attained prominent position among oxidising agents because of its commercial availability and is cheap and friendly oxidant. It can be used for the oxidation process directly or in combination with catalysts or with UV radiation. H_2O_2 readily undergoes reaction with hydrated electron from the water radiolysis reaction, that leads to formation of OH* radical **[8,9].**

$$H_2O_2 + e^-_{aq} \text{-------}\rightarrow OH^* + OH$$

Degree of degradation by addition of H_2O_2 increases with the greater attribution of OH* radical, as OH* radical formed degrade the dye chromophore efficiently **[10,11]**

However, some drawbacks have also been found with its use as it fails to oxidize some organic pollutants. It has been investigated by that removal efficiency for Methylene Blue dye was found to be 86% with this reagent **[12]** Hydrogen peroxide reagent is also found to be effective for the removal of Rhodamine dye with 99% efficiency as reported **[13].**

II.6.3. Using Fenton's Reagent

The mixture of hydrogen peroxide and ferrous ion (Fe^{+2}) is known as Fenton's reagent. Use of Fenton's reagent is one of the advanced oxidation process that has been examined for the removal of various dyes. This method involves oxidation of organic pollutants, following oxidatively degradation by hydroxyl radical that is generated from H_2O_2 in presence of Fe^{+2} as a catalyst.

$$Fe^{2+} + H_2O_2 \text{---------}\rightarrow OH^* + OH^-$$

A rapid reaction occurs between ferrous ion and H_2O_2 with the generation of radical hydroxyl. The efficiency of this process depends upon concentration of H_2O_2 and Fe^{2+} ions and on pH factor. As reported by some researchers, pH should be in between 3-5 **[14-16].**

The oxidation method using Fenton's reagent completely degrade the contaminants and break down them into harmless compounds like CO_2, H_2O and inorganic salts **[17].**

Moreover, this method is easy to carry out, completely reacts with organic compounds, is low cost treatment and do not produce any toxic compounds during the reaction. But, still then its applications has been found to be limited as generation of ferric hydroxide sludge in excess amount remains a disposal problem **[18]** This advanced oxidation method was found to be quite effective in case of Malachite Green dye with 99% removal efficiency as reported in the study **[19].** For the removal of Crystal violet dye removal efficiency has been found to be 98.2% with Fenton's reagent as reported in the literature **[20].**

II.6.4. Ozonisation Process

Ozone, known as the most powerful oxidant than other oxidizing agents like Cl_2, H_2O_2. Ozone is found to be quite capable in oxidizing chlorinated hydrocarbons, phenols and some other hydro carbons. The reaction mechanism involves two steps. Step 1 involves reaction occurring at pH value of 5-6, where ozone is present as in form of O_3 and undergoes reaction with double bond of dye molecules selectively. Step 2 involves reaction taking place at higher pH value i.e. above 8 pH, where ozone readily undergoes decomposition generating hydroxyl radicals that reacts non-selectively with organic compounds **[21].**

Ozonisation has been found successful in removing dyes from textile effluents **[22,23].** According to some researchers, reactive class of dyes show high extent of degradation with O_3 while, results found are moderate in case of basic dyes and poor results in case of disperse dyes [24]. The major advantage of this method is the application of ozone in its gaseous state and there is no sludge generation which makes it an effective tool of decolourization but, its high cost and short half-life are the barriers associated with ozonisation process **[21,25].**

II.7. Conclusion

The various studies show that dyes are among the most widespread pollutants due to their wide field of application. Their accumulation in stagnant water can generate many health problems, it is in this context that treatment techniques adapted to dyes come into play. Among the best methods that can be applied on this type of pollutants is adsorption using bio-adsorbent.

The adsorption technique is widely recognized as a vital path to removal of pollutants due to various technical merits: low material and operational cost, effective removal of diverse contaminants, basic infrastructure requirements, and simple to deploy for industrial applications.

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Chapter III: General informations on adsorption

III.1. Introduction

One of the techniques very frequently adopted for the treatment of water and industrial effluents is adsorption. Its principle is based on the property that solids have to fix on their surfaces.

III.2. Description of the adsorption phenomenon

Adsorption is a spontaneous surface phenomenon by which gas molecules or liquids are fixed on the surfaces of solids according to various more or less intense processes. The term surface corresponds to the entire surface of the solid, geometric surface for a non-porous solid, to which is added for a porous solid, the internal surface of the pores, accessible to the molecules of the fluid. It results in an increase in the density fluid at the interface of the two phases. It can therefore go from a few molecules on the surface, then a monolayer and up to several layers forming a true liquid phase **[1].**

We call "adsorbate" the molecule which is adsorbed and "adsorbent" the solid on which the molecule is adsorbed. The opposite phenomenon by which the molecules are detached is desorption **[2].**

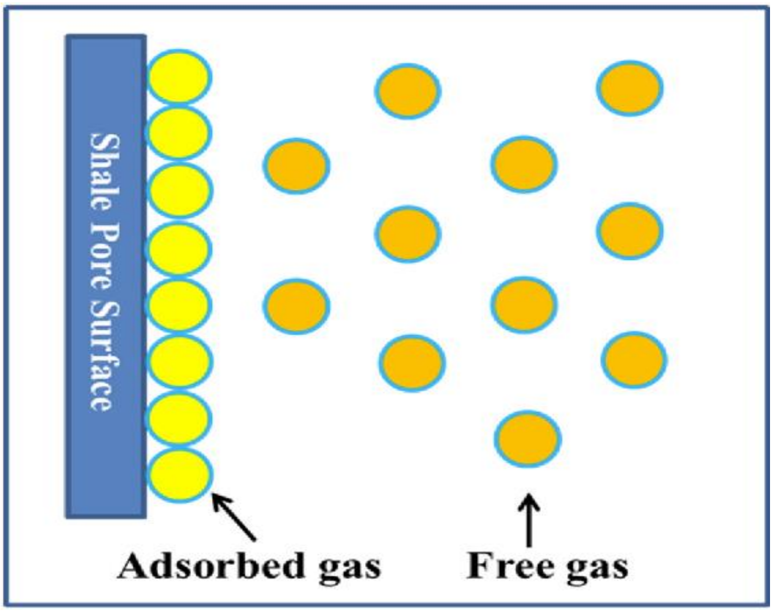

Fig. III.1. Adsorption phenomenon.

III.3. Adsorption characteristics

Depending on the nature and solidity of the fixing. If the adsorption leads to the creation of a true chemical bond between the fluid, we will speak of chemical adsorption or (chemisorption). If the fixation is purely the result of interaction forces, we distinguish two types of phenomenon, last physical, will use the term physical adsorption or (physisorption), the energies involved during this being generally much lower than chemisorption and more easily reversible **[3].**

III.3.1. Physical adsorption

Adsorption is called physical adsorption when it is due to physical interaction forces between the atoms, or groups of atoms of the solid and the molecules of fluid. These interactions are also called Van Der Waals forces. They are due to the movement of electrons inside molecules which can generate small instantaneous dipole moments. Electrostatic interactions can also combine with forces by Van Der Waals **[4].** Physisorption is of particular interest because it makes it possible to measure the surface specific to the adsorbent solid and the average pore size using criteria **[5].**

- The heat of adsorption released is around 20 KJ mol.
- The speed of the adsorption process is very fast.
- The quantity adsorbed decreases with the rise in temperature.
- Physical adsorption is completely reversible.
- The adsorption is done in several possible layers.

III.3.2. Chemical adsorption

In the case of chemical adsorption, there is creation of bonds between the atoms of the surface and the molecules of the adsorbate. Adsorption energies can be of the order of 200 KJ/mol. This type of adsorption is involved in the mechanism of heterogeneous catalytic reactions **[6].**

Chemisorption is complete when all the active centers present at the surface have established a bond with the adsorption molecules. Table 1 presents the typical differences in adsorption.

Table.III.1. Differences between physical adsorption and chemical adsorption.**[9]**

Properties	***Physical adsorption***	***Chemical adsorption***
Adsorption energy	5 to 10 Kcal/mol	20 to 100 Kcal/mol
Process's temperature	Below equilibrium temperature	High
Nature of links	Physical (Fan Der Waals)	Chemical
Desorption	More or less perfect	Difficult
Activation energy	Not noticeable	Can be put into play
Kinetics of reactions	Very fast	Slow
Surface condition	Formation of multilayers	Formation of monolayer

III.4. Mechanism of adsorption

Adsorption is a universal surface phenomenon by which a solid fixes the molecules of a body on its surface. In most cases, the phenomenon of adsorption takes place between a gas and the surface of a solid. The adsorption process can be divided into four steps:

Step 1: Transfer of the particle (Very fast).

Step 2: Displacement of the bound water until it is in contact with the adsorbent (Fast).

Step 3: Diffusion inside the adsorbent under the influence of the concentration gradient (Slow).

Step 4: Adsorption in a micropore (Very slow).

The activity level of the adsorption is based on the concentration of the substance in water, the temperature and the polarity of the substance. The phenomenon of adsorption, controlled by the diffusion of molecules, reaches its balances relatively quickly. But, can be prolonged over very long times for microporous adsorbents due to the slowing diffusion of molecules in these structures of dimensions close to the diameter of the fluid's molecules **[10]**. Adsorption is less effective against polar solvents and chlorine compounds with low molecular charge. Adsorption of ionized compounds is low.

III.5. Factors influencing the phenomenon of adsorption

When a solid is brought into contact with a solution, each constituent of the latter, the solvent and the solute, shows a tendency to adsorption on the surface of the solid. So, there is a competition on the surface between two adsorptions which are competitive **[7].**

The most interesting case is when the adsorption of the solute is far greater than that of the solvent. So, the amount adsorbed depends on many factors, the main ones are:

III.5.1. Factors characterizing the adsorbate

Not all substances are adsorbable in the same way. The retention capacity of a pollutant is a function the binding energy of the substance to be adsorbed, due to its structure and size of the molecules, a high molecular weight reduces the diffusion and therefore the fixation of the adsorbate of its solubility, the less soluble a substance is, the better it is adsorbed from its concentration. In general, the nature of the adsorbate is described by two rules:

- Lundeluis rule: "the less a substance is soluble in the solvent, the better it is adsorbed", it can be said that the less hydrated and polarizable ions are the most strongly adsorbed
- Traube's rule: "the adsorption to aqueous solutions increases when one goes through a series of homologs".

III.5.2. Factors characterizing the adsorbent

An adsorbent solid is characterized by physicochemical, mechanical and geometric properties, the most important are the geometric properties.

- **The specific surface:** The specific surface is an essential data for the characterization of solids and porous materials. It is clear that the aim is to give the adsorbents a large specific surface. This quantity designates the accessible surface in relation to the unit weight of adsorbent. To achieve a significant adsorption effect, it is necessary that the surface of the adsorbent is as large as possible.**[11].**
- **The structure of the adsorbent:** Adsorption of a substance increases with decreasing particle size and pore size of the adsorbent. However, if the diameter of the pores is less than the diameter of the molecules. The adsorption of this compound will be negative, even if the surface of the adsorbent has a high affinity for the compound. The pore size distribution plays an important role in the overall kinetics of the adsorption process.
- **Polarity:** Polar solids preferentially adsorb polar bodies, and apolar solids adsorb apolar bodies. The affinity for the substrates increases with the molecular mass of the adsorbate. The adsorption is more intense for the bodies, which have relatively more affinity for the solute than for the solvent.
- **Temperature:** The amount adsorbed at equilibrium increases when the temperature decreases, moreover, adsorption releases heat of adsorption like any exothermic reaction, it is therefore favored by low temperatures.**[12].**
- **pH:** Sometimes pH has a significant effect on adsorption characteristics.**[13]** Adsorption is maximum at isoelectric as well, a neutral molecule is better adsorbed than another, the adsorption of basic dyes, such as methylene blue is all the better as the pH is high. Beyond pH = 8, OH ions seem to undergo dye desorption.

III.6. Adsorption isotherms

Solute adsorption is generally limited to the monolayer. Indeed, solid solute interactions are strong enough to successfully compete with solid solvent interactions in the monolayer. However, this is no longer the case in the following layers **[8].**

The adsorption of the solute in multilayer was observed in certain cases, based on the shape of the isotherms established and on the fact that the specific surface, evaluated from the assumption of a monolayer, is too low. Such an isotherm is a curve which represents the relationship between the quantity adsorbed per unit mass of solid and the concentration of the fluid phase.

Such a curve is obtained from the results of tests carried out at a constant temperature. To do this, quantities of solid are introduced into volumes of solution to be treated, and after a given contact time, the residual concentration of the solution.

The quantity adsorbed can be calculated using the following equation:

$$q_e = \frac{C - C_e}{m} \times V$$

Where: C: initial concentration of the metal in (mg/L), Ce: concentration of the metal at equilibrium in the solution in (mg/L), m: mass of adsorbent (g), q_e: quantity adsorbed per unit mass of the adsorbent in (mg/g), V: volume of the solution (L).

The least important isotherms are those of Langmuir, which are based on rarely satisfactory hypotheses, particularly with regard to the homogeneity of the surface but they remain the most used.

The Freundlich isotherm is quite close to that of Langmuir at concentrations averages. Both Langmuir and Freundlich models are suitably applied for monolayer adsorption. On the other hand, the Brunauer, Emmet and Teller (BET) isotherm are better suited to multilayer adsorption.

III.6.1. Langmuir isotherm

The Langmuir isotherm was proposed in 1918. It is a simple and widely used model, based on the assumptions below:

- There are several adsorption sites on the surface of activated carbon.
- Each of these sites can adsorb a single molecule; therefore, only one layer of molecules can be adsorbed by the activated carbon.
- Each site has the same affinity for impurities in solution.
- Activity at one site does not affect activity at adjacent sites

The development of Langmuir's representation, for a chemical adsorption isotherm, relies on a number of assumptions:

- The surface of the solid is uniform.
- The heat of adsorption is independent of the rate of coverage of the solid surface.
- The adsorption is localized and only gives rise to the function of a monolayer.
- There is equilibrium between the molecules of the two phases.

The Langmuir model gives several types of isotherms which are related quite precisely to various modes of fixation of the adsorbent.

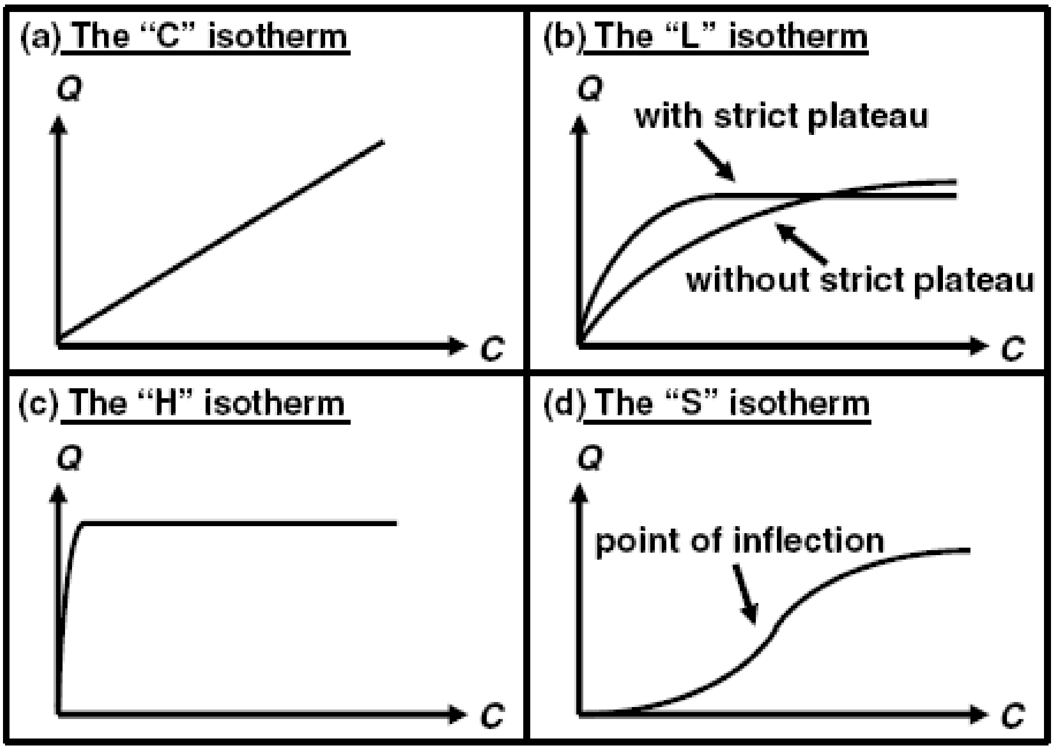

Fig. III.2. The different types of Langmuir isotherms.

From Fig.III.2, four types of Langmuir isotherms are distinguished.

- **Type** L: Indicates vertical adsorption of polar monofunctional molecules on a polar adsorbent. Here, the solvent competes with the solute for the occupation of the adsorbent sites.
- **Type S:** Normal Langmuir type, indicates flat adsorption of bifunctional molecules. In this case the adsorption of the solvent is weak and that of the solute on the solid is done in monolayer
- **Type H :** Does not start at zero but a positive value, indicates a high affinity often observed for solutes adsorbed in the form of micelles. This means that at low concentrations, adsorption is complete.
- **Type C :** Straight line means it has competition between solvent and solute to occupy the sites, always with the same sharing.

III.6.2. Freundlich isotherm

In 1926, Freundlich established a very satisfactory isotherm which can be applied successfully to adsorption, but which has been used mainly for solution adsorption.

III.6. 3. Temkin isotherm

Temkin assumes that the lowering of the heat of adsorption with the increase in the recovery rate is not logarithmic as in the case of the systems leading to the Freundlich equation, but linear in particular at medium and low recovery rates. This linearity may be due to:

- The repulsion between adsorbed species on the uniform surface.
- Surface heterogeneity.

III.6.4. Isotherm of BET (BRUNAUER, EMMETT, TELLER)

The BET hypothesis is based on the formation of the multilayers. Molecules arise on top of each other to give an interfacial zone which can contain several thicknesses of sorbed molecules. This model admits the formation of multilayers of adsorbate, a homogeneous distribution of the sites of the surface of the adsorbent and the existence of an energy of adsorption which retains the first layer of adsorbed molecules and a second energy which retains the layers next The model also takes into account the phenomenon of saturation and involves the solubility of the solute in its solvent, in the form of the saturation concentration Cs.

The isotherm of (BET), proposed in 1938, is based on the assumptions below:

- Several successive layers of molecules can be fixed on the adsorbent * Adsorption sites are uniformly distributed on the surface of the adsorbent.
- Each site is independent of neighboring sites.

III.7. Types of adsorbents

Adsorption is a surface phenomenon, hence the interest in knowing the physical properties of adsorbent materials such as porosity, specific surface area, apparent and real density.

III.7.1. Activated carbons

Activated carbons are prepared by pyrolysis of a material containing carbon, coal or plant material, to produce a charcoal which is then oxidized by water vapor under controlled conditions to create a microporous structure. There are several hundred qualities of activated carbon, depending on the precursor and the treatment conditions. One can also find so-called "chemical" activated carbons, because activated when hot in the presence of dehydrating chemical agents, phosphoric acid or zinc chloride. These are hydrophobic adsorbents with a specific surface area between 500 and 1500 m^2/g. Their porosity, their vast field of application and their cost make activated carbons the most widespread adsorbents.

III. 7. 2. Mineral adsorbents

Mineral adsorbents can exist naturally or synthesized.

III.7.2.1. Clays

Clays are aluminosilicates. These are natural products, which are activated to have better adsorbent properties

III.7.2.2. Zeolites

Zeolites are adsorbents with a three-dimensional aluminosilicate crystalline skeleton consisting of SiO_4 and AlO_4 tetrahedra, with the overall formula (AlO_2, $nSiO_2$) where M most often represents an alkali or alkaline-earth metal and $n \geq 1$. There are more than 100 species of zeolites, differing in the value of n and the microporous structure made of cavities and channels which gives them adsorbent properties.

III.7.2.3. Activated aluminas

Activated aluminas are obtained by flash thermolysis of aluminum trihydroxide $Al(OH)_3$ which leads to a product of approximate composition Al_2O_3, 0.5 H_2O, possessing a porous structure resulting from the departure of water molecules. The surface of the pores is covered with Al-OH groups, and the adsorption takes place preferentially by hydrogen bonding. Activated aluminas are amorphous, moderately polar and hydrophilic adsorbents. They have a specific surface of 300 m²/g.

III.7.2.4. Silica gels

Silica gels are prepared from $Si(OH)_4$ in the aqueous phase, obtained by acidification of a sodium silicate, or from a silica sol The Si-OH groups lead to hydrogen bonds.

There are two types of silica gels, the microporous, quite hydrophilic, and the macroporous, versatile, which differ in pore size as the name suggests. Their specific surface can be from 300 to 800 m²/g.

III.7.3. Polymer-based adsorbents

These are mostly products in development which currently only have very specific and few applications. The most common is a copolymer of styrene and divinylbenzene polystyrene forms chains linked together by bridges of divinylbenzene, which gives inter-chain porosity to the structure. An important characteristic of these adsorbents is that they are very hydrophobic. These products can be used as is or undergo carbonization. We then obtain adsorbents similar to activated carbons If the initial polymer is prepared in fibers, we can weave it and obtain activated carbon fabrics.

The fiber diameter being of the order of 10 microns, the transfer time is much longer faster than for all other adsorbents. Its specific surface can reach for activated carbon fabrics 2000 m²/g.

III.8. Conclusion

The phenomenon of adsorption has the advantage of being able to be applied to the treatment of various effluents. The modeling of adsorption isotherms makes it possible to provide thermodynamic information on the specific surface and the porous structure of the solid, which are two parameters that influence adsorption.

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GENERAL CONCLUSION

This research paper was aimed at comparing the applicability of CCD and BBD for the optimization of initial concentration, pH, temperature and biosorbents dose in determining their desirability efficiency in a crystal violet for the treatment of wastewaters.

The presence of crystal violet dye in the industrial effluents is an environmental concern, and therefore it's removal is inevitable. Biosorbents were utilised for the removal of dye from aqueous solution through adsorption process. The purpose of the present study was to examine and optimize the effect of initial dye concentration, pH, temperature and adsorbent dose on dye adsorption Central Composite Design (CCD) and Box-Behnken Design (BBD). The experimental data were used as input in the Central Composite Design (CCD) and Box-Behnken Design (BBD). The optimum values obtained for initial dye concentration, pH, temperature, adsorbent dose and maximum adsorption capacity were 100 mg/L, pH6, 40 °C, 0.025 g, 169.711 mg/g (MM1) and 170.563 mg/g (MM2) for Box-Behnken Design and 100 mg/L, pH6, 40 °C, 0.025 g, 179.39 mg/g (MM1) and 183.292 mg/g (MM2) for Central Composite Design, respectively.

Central Composite Design was found to be better in comparison to Box-Behnken Design for the optimization of crystal violet dye adsorption onto biosorbents.