1.1- Introduction

The earth is the only planet in the whole universe, which is accredited to have life. One of the main reasons, which support life in our mother planet is water. But, anthropogenic activities have caused a great harm to the quality of our lifeline, i.e. water. Because of the fast depletion of the freshwater resources, removing pollutants from water is the crying need.

A dye is a colored substance that has an affinity to the substrate to which it is being applied. Dyes appear to be colored because they absorb some wavelengths of light more than others. Humans are estimated to use dyes for thousands of years and the earliest use of the colorant is believed to be by Neanderthal man about 1800 years ago [1, 2]. The year 1856 witnessed a historic discovery of first synthetic dye [3, 4]. In due course of time, these synthetic dyes gained huge popularity and began to be synthesized on a large scale. In fact, it has reached to a level of annually, over 7.0×10^5 tones and nearly 100,000 different types of dyes are produced worldwide [5].

1.2- Environmental problems

The extensive use of chemicals for various purposes in day-to-day life and the growing industrialization led to unwanted contamination of our existing natural resources by the release of diverse organic and inorganic pollutants into water system [6]. Various pollutants contained in industrial wastewaters, dye is considered to be very important from the aesthetic point of view and is stated as visible pollutant. Dyes usually have a synthetic origin and complex aromatic molecular structures, which make them more stable and more difficult to biodegrade and are widely used in textiles, paper, plastic, leather, cosmetics and food industries to color their products. The extensive use of dyes often caused pollution problems in the form of colored wastewater discharged into environmental water bodies. High concentrations of textile dyes in water bodies may stop the reoxygenation capacity of the receiving

water and cutoff sunlight thereby upset the biological activity in aquatic life and also the photosynthesis process of aquatic plants or algae[7].

1.3- Background of Present Research

Now a days, a large amount of wastewater has a color is that generated by many industries like textile, leather, paper, printing, plastic and so on [8]. The presence of dye materials greatly influence the quality of water and the removal of this kind of pollutant is prime importance. Owing to their complicated chemical structures, dyes are difficult to be treated with municipal waste treatment operations [5]. Even a small quantity of dye does cause high visibility and undesirability. Moreover, the color produced by dyes in water makes it aesthetically unpleasant [8]. They have acute or chronic effects on exposed organisms, which depend on the concentration of the dye and the exposed time [5]. In addition to that, many dyes are considered to be toxic and even carcinogenic [8-10].

1.4- Toxicity of Dyes:

Several dyes cause damage of DNA that can lead to the genesis of malignant tumors. Some of the best known dyes and their breakdown derivatives inducing cancer in humans and animals are benzidine and its derivatives, and also a large number of anilines. In different toxicological studies indicated that 98% of dyes has a lethal concentration value for fishes higher than 1 mg/L, and 59% have an value higher than 100 mg/L (31% of 100-500 mg/L and 28% higher than 500 mg/L) [11].

In addition to being toxic, dye effluents also contain chemicals that are carcinogenic, mutagenic or teratogenic to various organisms. This is especially serious because many chemicals can cause damage to genetic material without being expressed immediately. Azo and nitro compounds have been reported to be reduced in sediments of aquatic bodies giving rise to potentially carcinogenic amines. Many dyes are made from known

carcinogens like benzidine and are also known to accumulate, thus posing a serious threat. Many dyes are also known to get reduced to toxic substances inside living organisms [12].

1.5- Techniques available for color removal

1.5.1- Biological treatments

Biological treatment is often the most economical alternative when compared with the other physical and chemical processes. Biodegradation methods such as fungal decolorization, microbial degradation, adsorption by (living or dead) microbial biomass and bioremediation systems are commonly applied to the treatment of industrial effluents because many microorganisms such as bacteria, yeasts, algae and fungi are able to accumulate and degrade different pollutants[13]. However, their application is often restricted because of technical constraints. Biological treatment requires a large land area and is constrained by sensitivity toward diurnal variation as well as toxicity of some chemicals, and less flexibility in design and operation [14].

1.5.2- Chemical methods

Chemical methods include coagulation or flocculation combined with flotation and filtration, precipitation flocculation with $Fe(II)/Ca(OH)_2$, electroflotation, electrokinetic coagulation, conventional oxidation methods by oxidizing agents (ozone), irradiation or electrochemical processes. These chemical techniques are often expensive, and although the dyes are removed, accumulation of concentrated sludge creates a disposal problem. There is also the possibility that a secondary pollution problem will arise because of excessive use of chemicals. Recently, other emerging techniques, known as advanced oxidation processes, which are based on the generation of very powerful oxidizing agents such as hydroxyl radicals, have been applied with success for pollutant degradation. Although these methods are efficient for the treatment of water contaminated with pollutants, they are very costly and

commercially unattractive. The high electrical energy demand and the consumption of chemical reagents are common problems.

1.5.3- Physical methods

Different physical methods are also widely used, such as membrane-filtration processes (nanofiltration, reverse osmosis, electrodialysis). The major disadvantage of the membrane processes is that they have a limited lifetime before membrane fouling occurs and the cost of periodic replacement must thus be included in any analysis of their economic viability. In accordance with the very abundant literature data, adsorption techniques liquid-phase adsorption is one of the most popular methods for the removal of pollutants from wastewater since proper design of the adsorption process will produce a high-quality treated effluent. This process provides an attractive alternative for the treatment of contaminated water, especially if the sorbent is inexpensive and does not require an additional pre-treatment step before its application. Adsorption is a well known equilibrium separation process and an effective method for water decontamination applications [15]. Adsorption has been found to be superior to other techniques for terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants.

1.6- Principles of Adsorption

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid, forming a molecular or atomic film. In other words, adsorption is the adhesion of atoms, ions, biomolecules or molecules of gas, liquid, or dissolved solids to a surface and this process creates a film of the adsorbate (the molecules or atoms being accumulated) on the surface of the adsorbent. It is a surface phenomenon and a consequence of surface energy. The atoms on the surface of the adsorbent are not wholly surrounded by the other atoms and thus, can attract adsorbates.

The exact nature of the bonding depends on the details of the species involved, but the adsorption process is generally classified as follows:

1.6.1- Physical adsorption:

Physical adsorption is called natural adsorption, which means the surface adsorption of particles. It is produced by natural forces that challenge the surface of the atom. The value of adsorption temperature is one of the best criteria used for the distinction between the two types of physical adsorption and chemical adsorption. It is value in physical adsorption is less than 40 kilojoules. It is limited in normal conditions and at low temperatures. The particles or atoms absorbed in this type have the ability to move within a specific area. Physical adsorption can be limited to temperatures approaching or below the boiling point of the absorbent material when appropriate conditions are available. [16,17].

1.6.2- Chemical adsorption:

This type of adsorption is restricted to active, unsaturated surfaces electronically. When the material is absorbed in several layers on the solid surface, it is called a multi-particle. Chemical adsorption is more specific, which can be limited to certain surfaces and not to another surface when these same conditions changed. The chemical adsorption is the first step in the chemical reaction, so it needs high activation energy. The characteristic minutes require a constant activation energy for the homogeneous surface and can vary. The energy of activation from one location to another on the same surface as when it is not homogeneous. The chemical adsorption consists of a single layer of material that is highly absorbent on the surface. Chemical adsorption is limited to temperatures greater than the boiling point of the absorbent material, therefor , the temperature plays an important role in the adsorption process [16,17].

1.7- Adsorption Mechanism:

Adsorption occurs in three steps. First step, the adsorbate diffuses from the major body of the stream to the external surface of the adsorbent particle. Second step, the adsorbate migrates from the relatively small area of the external surface to the pores within each adsorbent particle. The bulk of adsorption usually occurs in these pores because there is a majority of available surface area. Final step, the contaminant molecule adheres to the surface in the pore. This overall diffusion and adsorption process is illustrated in Figure (1.1) [18].

Contaminant molecules
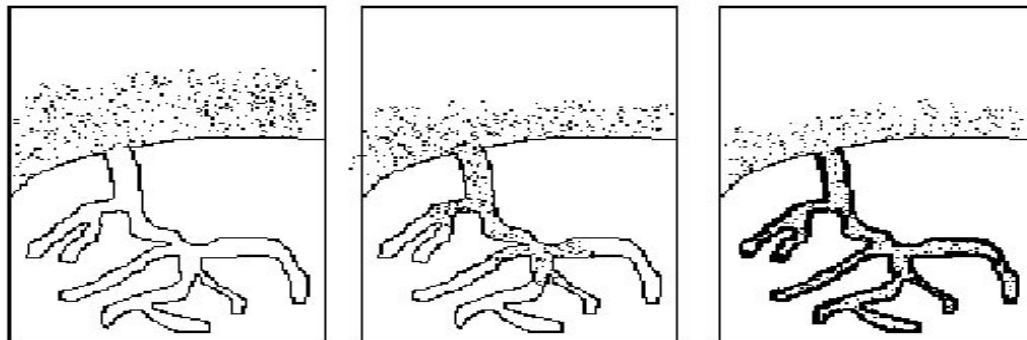
Step 1: Diffusion to   Step 2: Migration into   Step 3: Layer Build up
Adsorbent Surface   Pores of Adsorption   of adsorbate.

Figure (1.1) Mechanism of Adsorption [18].

1.8- Adsorption Isotherms:

Adsorption isotherm expresses the quantity of material adsorbed per unit mass of adsorbent as a function of the equilibrium concentration of the adsorbate. The necessary data are derived from experiments where a specified mass of adsorbent is equilibrated with a known volume at a specific concentration is measured in solution by the mass balance equation(1.1):

$$q_e = \frac{(C_0 - C_e) \times V}{m} \qquad \dots (1.1)$$

Where,

$q_{e=}$ The adsorption density mg of adsorbate per g of adsorbent.

C_0 = The concentration of adsorbate in solution mg/L.

C_e = Final equilibrium concentration of adsorbate after adsorption has occurred, mg/L.

V= Volume of liquid in the reactor, (L).

m = mass of adsorbent, (g).

1.9- Adsorption Equilibrium and the Adsorption Isotherm:

Positive adsorption in a liquid-solid system results in the removal of solutes from solution and their concentration at the surface of the solid, to such time as the concentration of the solute remaining in solution is in a dynamic equilibrium with that at the surface. At this position of equilibrium, there is a defined distribution of solute between the liquid and solid phase [19]. In general, the adsorption isotherm describes how adsorbents will interact with adsorbents and so is critical in optimizing the use of adsorbents [20].

The Langmuir isotherms monolayer coverage of adsorbate over a homogenous adsorbent surface. Graphically, a plateau characterizes the Langmuir isotherm. Therefore, at equilibrium, a saturation point is reached where no further adsorption can occur. Adsorption is assumed to take place at specific homogenous sites within the adsorbent. Once a dye molecule occupies a site, no further adsorption can take place at that site [21].

Langmuir equation is given in equation (1.2) [20].

$$q_e = \frac{(C_0 - C_e) \times V}{m} \qquad \dots(1.1)$$

Rearranging Equation (1.1), we have:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_l} + \frac{1}{q_m} C_e \qquad \dots(1.2)$$

7

where q_m shows the monolayer adsorption capacity (milligrams per gram), K_l Langmuir constant (liters per milligram), C_e equilibrium concentration of adsorbate in the solution (milligrams per liter), and q_e the solid phase concentration of adsorbate at equilibrium (milligrams per gram).

Therefore, by plotting C_e/q_e against C_e it is possible to obtain the value of q_m from the slope, which is $(1/q_m)$ and the value of K_l from the intercept which is $(1/K_l q_m)$. The Langmuir Equation is applicable to homogenous sorption where the sorption of each molecule has equal sorption activation energy [21].

The equation is thermodynamically consistent and follows Henry's Law at concentration approaching zero [20]. The essential characteristics of the Langmuir Equation can be expressed in terms of a dimensionless factor, R_L, which is given below:

$$R_L = \frac{1}{1 + C_0 K_L} \qquad \text{... (1.3)}$$

The value of the isotherm to be either;

- Unfavorable $(R_L > 1)$
- Linear $(R_L = 1)$
- Favorable $(0 < R_L < 1)$
- Irreversible $(R_L = 0)$ [20].

The freundlich Expression given in equation (1.4):

$$\ln q = \ln k + b \ln C_e \qquad \text{…(1.4)}$$

Is an exponential equation and therefore, assumes that as the adsorbate concentration increases so does the concentration of adsorbate on the adsorbent surface. Theoretically, using this expression, an infinite amount of adsorption can occur.

$$q_e = K_f C_e^{\frac{1}{n}} \qquad \qquad …(1.5)$$

The expression is characterized by heterogeneity factor, $\frac{1}{n}$ and so the Freundlich isotherm may be used to describe heterogeneous systems [21]. For favorable adsorption, value of $\frac{1}{n}$ must be between 0 and 1 [22]. The Freundlich isotherm agrees well with the Langmuir over moderate concentration ranges but, unlike the Langmuir expression, it does not reduce to the linear isotherm (Henry's Law) at low surface coverage. Both these theories suffer from the disadvantage that equilibrium data over a wide concentration range cannot be fitted with a single set of constants [21]. To determine the constants K_f and $\frac{1}{n}$, the linear from Equation (2) shown below may be used to produce a graph of $\ln(q_e)$ against $\ln(C_e)$

$$\ln q_e = \ln K_F + \frac{1}{n} \ \ln C_e \qquad \qquad …(1.6)$$

1.10- Dyes:

Over 700,000 tones dye stuff are produced annually estimated to consist of more than100,000 commercially available dyes. Mauveine was the first modern synthetic organic dye discovered by chance by William Henry Perkin in London in 1856. Actually, this dye was neither the first synthetic dye to be produced in the laboratory nor even the first to be manufactured. The first synthetic organic dye was picric acid, which had been manufactured in 1845 by nitrating phenol [23].

In 1875, the dye chemist Otto N. Witt proposed a color theory and constituted that a compound is colored due to the presence of certain arrangements of atoms or groups, called chromophores. And the other groups called auxochromes enable the dye to bond to fibres and modify the color. Dyes are colored compound used to impart its color to a substrate material of which it becomes an integral part by one of the various processes dyeing, printing, and

surface coating. Generally, the substrate includes textile fibres, polymers, foodstuffs, oils, leather, and many other similar materials [24].

The major components of dye molecules are chromophores and auxochromes. A chemical structure which is colored is normally accomplished in the synthesis of dyes using a chromogen -chromophore with an auxochrome. The chromophore group is a 'color giver' which forms a basis for the chemical classification of dyes when coupled with the chromogen. The most important chromophores are azo (–N=N-), carbonyl (-C=O), and nitro (-NO$_2$) groups.[25]

1.11- Classification systems for dyes:

Dyes can be grouped in accordance with two different principles:

a)-Chemical structure (chemical classification) .

b)-Dyeing methods areas of application (coloristic classification).

A review of the whole field of technical dyes shows that two classifications overlap that there is hardly a chemical class of dye, which occurs solely in one coloristic group, and vice versa [26] .

Dyes are classified as anionic, cationic and nonionic. Anionic dyes are the direct, acid and reactive dyes. A cationic dye is basic dyes; while a nonionic dye is disperse dyes. Nonionic dyes refer to disperse dyes because they do not ionize in an aqueous medium. The chromophores in anionic and nonionic dyes are mostly azo groups or anthraquinone types. Table (1.1) summarized the application classes of dyes and their chemical type.

Table (1.1) Application Classes of Dyes and Their Chemical Types.

Class	Substrate	Method of Application	Chemical types
Acid	Nylon, wool, silk, paper, inks and leather.	Usually from neutral to acidic bath.	Azo (including premetallized), anthraquinone, tryphenylmethane, azine, xanthene, nitro and nitroso.
Basic	Paper, polyacrylonitrile, modified nylon, polyester and inks.	Applied from acidic dye baths.	cyanine, hemicyanine, diazahemicyanine, diphenylmethane, triarylmethane, azo, azine, xanthene, acridine, oxazine and anthraquinone.
Reactive	Cotton, wool, silk and nylon.	Reactive site on dye reacts with functional group on fiber to bind dye covalently under influence of heat and pH (alkaline).	Azo, anthraquinone, phthalocyanine, formazan, oxazine and basic.
Direct	Cotton, rayon, paper, leather and nylon.	Applied from neutral or slightly alkaline baths containing additional electrolyte.	Azo, phthalocyanine, stilbene, and oxazine.
Disperse	Polyester, polyamide, acetate, acrylic and plastics.	Fine aqueous dispersions often applied by high temperature/pressure or lower temperature carrier methods; dye maybe padded on cloth and baked on or thermo fixed.	Azo, anthraquinone, styryl, nitro and benzodifuranone.
Solvent	Plastics, gasoline, varnishes, lacquers, stains, inks, fats, oils, and waxes.	Dissolution in the substrate	Azo, triphenylmethane, anthraquinone, and phthalocyanine
Vat	Cotton, rayon and wool	Water-insoluble dyes solubilized by reducing with sodium hydrogensulfite, then exhausted on fiber and reoxidized	Anthraquinone (including polycyclic quinines) and indigoids

1.12- Disadvantages of dyes:

Dyes are sometimes being viewed as something more than ordinary chemical. But, actually it is an individual chemical itself like all other chemicals such as sodium chloride, acetic acid and benzidine. They are similar in their reactions to other some chemicals, and distinctly different from others. Therefore, there is a possibility that they are toxic. This is because many dyes are made from known carcinogens, such as benzidine and other aromatic compounds [26]. Additionally they also can cause severe damage to human beings such as dysfunction of kidney, reproductive system, liver, brain and central nervous system .Table 1.2 shows the disadvantages according to different dye class.

Table (1.2) Disadvantages of different dye class.

Dye class	Disadvantages
Azo groups	Their reductive cleavage of azo linkages is responsible for the formation of toxic amines in the effluent.
Anthraquinone-based dyes	It is the most resistant to degradation due to their fused aromatic ring structure and thus remains coloured for a longer time in wastewater.
Basic dyes	It has high brilliance and intensity of colours and is highly visible even in a low concentration.

1.13-Methylene blue Crystal Violet and Methyl Green dyes:

1.13.1-Methylene blue (MB):

The methylene blue Caro discovered dye in 1878. It is a basic cationic dye, heterocyclic aromatic chemical compound with molecular formula: $C_{16} H_{18} N_3SCL$, Molecular Weight=319.85. Melting point 100 to 110 °C

(with decomposition). With an absorbance maximum λmax = 663nm. It has many uses in a range of different fields, such as biology or chemistry and in textile industries. At room temperature, it appears as a solid, dark green powder, which yields a blue solution when dissolved in water. Methylene blue is highly stable in the human body, and if ingested, it resists the acidic environment of the stomach as well as the many hydrolytic enzymes present. It is not significantly metabolized by the liver, and is instead quickly filtered out by the kidneys. Therefore, it is necessary to make sure that the effluent contained methylene blue was treated first before releasing it to environment, it is used in textile laboratories and is considered an environmental pollutant.[18] Figure (1.2) shows the structural structure of the methylene blue dye.
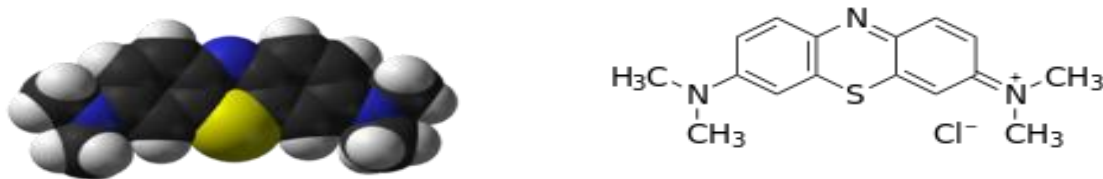
Figure (1.2) structure of methylene blue [62].

1.13.2-Crystal violet (CV):

Crystal violet is one of the components of methyl violet, a dye that was first synthesized by Charles Lauth in 1861, when dissolved in water the dye has a blue-violet colour with an absorbance maximum at 590 nm. Chemical formula $C_{25}H_{30}ClN_3$, molar mass 407.99 g·mol^{-1}, melting point is 205 °C. Hazardous in case of ingestion or inhalation. Slightly hazardous in case of skin contact (irritant). It may affect genetic material (mutagenic) and may cause adverse reproductive effects and birth defects based on animal test data. It may cause cancer based on animal test data. It can stain the area of contacted skin, Crystal violet is used to dye paper and as a component of navy

blue and black inks for printing, ballpoint pens and printers. It is used to colorize diverse products such as fertilizers, anti-freezes, detergents, and leather jackets. The dye is also used as a histological stain[63].
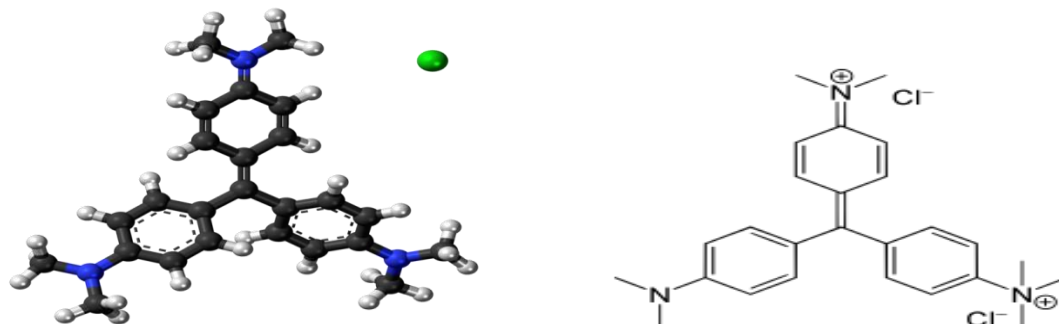

Figure (1.3) Structure of Crystal Violet [63].

1.13.3-Methyl Green (MG):

Methyl green is peculiar among cationic (basic) dyes in having two positive charges on the cation [27]. The structural formula is shown in fig.(1.5). Methyl green dye is used in chemical laboratories, as a detector and as a medium to conduct various reactions in the blood. It might be harmful if inhaled and causes irritation of the respiratory system and if absorbed through the skin, It causes irritation of the skin and the eye, and it is also harmful if swallowed. When dissolved in water the dye has a blue-green colour with an absorbance maximum at 631.85 nm. Chemical formula $C_{27}H_{35}BrClN_3 \cdot ZnCl_2$, formula weight 458.5. melting point 300°C.
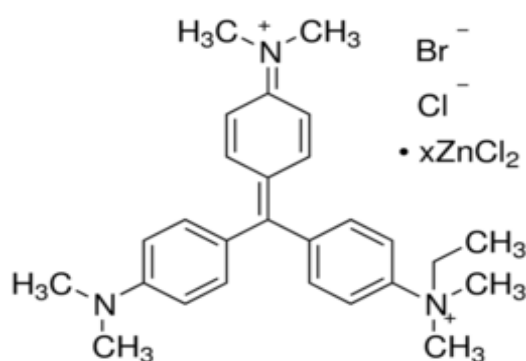

Figure (1.4) Structure of Methyl Green[64].

1.14- SEAWEED:

Biologically, seaweeds are classified as macroalgae, with subclassification as brown (Phaeophyta), red (Rhodophyta) or green algae (Chlorophyta). In 1994/95, over 2,000,000 tones (dry weight) of seaweed was harvested. Much of this may be consumed as whole seaweed products, while a large proportion is also used in the production of over 85,000 tones of viscous polysaccharides for various food and industrial applications [28].

Macroalgae or seaweeds belong to one of several groups of multicellular algae: red algae, green algae, and brown algae. Macroalgae can be used as nonliving biomasses to remove various textile dyes. Hence, Macroalgae are nontoxic, low-cost, and easily available biomaterials for the treatment of colored effluents. The cell wall of marine macroalgae has a good binding affinity due to the presence of proteins, polysaccharides, and lipids on the surface that act as binding sites. The biosorption depends on the chemical characters of the pollutant, type of material, and environmental conditions. [29]. In spite of the scarcity of consistent cost information, the widespread uses of low-cost adsorbents in industries for wastewater treatment applications today are strongly recommended due to their local availability, technical feasibility, engineering applicability, and cost-effectiveness. If low-cost adsorbents perform well in removing MB, CV, and MG at a low cost, they can be adopted and widely used in industries not only to minimize cost-inefficiency but also to improve profitability.

1.15- Literature Reviews:

N.M.Mahmoodi, et al., studied dye removal from colored textile wastewater using chitosan in binary system was studied [30]. Here, Direct Red 23 and Acid Green 25 were used as anionic dyes. The adsorption kinetics of dyes on chitosan followed the pseudo second order at different pH values. The experimental data were correlated reasonably well by Tempkin adsorption isotherm. It was concluded that the chitosan is an eco- friendly adsorbent for dye removal from low concentration of acidic colored textile wastewater.

S.A.Saad, et al., studied chemically modified sugarcane bagasse as a potentially low-cost biosorbent for the removal of methyl red was studied [31]. The kinetics of methyl red adsorption followed the pseudo first order kinetic expression and Langmuir isotherms model fit well. From the study, it was inferred that sugarcane bagasse has a good potential to be used for small scale industries, which produces dyes as their effluent, after it was being pretreated with phosphoric acid.

S.Chakrabarti, et al., studied active manganese oxide as a treatment of wastewater containing congo red [32]. The equilibrium data was very well represented by the Langmuir and Freundlich isotherms as well as a pseudo second order kinetic model.

A. Mital, et al., studied coconut and coffee husks were identified as potential biosorbents for removal of hazardous dye, Quinoline yellow [33]. The equilibrium data fitted well to the pseudo first order model and conform to the Langmuir and Freundlich isotherms. The results also showed that the reaction was exothermic.

D.Sun, et al., studied the removal of reactive red 23, reactive blue 171, acid black 1 and acid blue 193 from aqueous solution using fly ash [34]. The

results showed that adsorption was pH dependent, adsorption increased with the initial dye concentration; the reaction was spontaneous and exothermic in nature.

Krishna Bahadur Dawadi1, et al., studied adsorptive removal of methyl red (MR) from aqueous solution onto chemically modified Charred Sal (Shorea robusta) Saw-Dust (CSSD) and Xanthated Sal Saw-Dust (XSSD) has been investigated. The surface modification is characterized by Fourier transformed infra-red (FTIR) spectroscopy, scanning electron microscopy (SEM) and elemental Analysis. Different parameters are studied such as contact time, optimum pH, and initial ion concentration. Maximum dye removal is observed at pH 4 for charred and xanthated Sal saw dust. The dye can be quantitatively removed onto the surface of these adsorbent. At a contact time of 3-4 hours maximum adsorption capacity (qmax) for CSSD and XSSD were found to be 70 mg/g and 130 mg/g respectively. Adsorption kinetic data were best fitted onto pseudo second order. [35].

Md Shariful Islam1, et al., studied Adsorption capability of activated carbon synthesized from coconut shell. Activated carbon was synthesized from coconut shells. The field emission scanning electron microscopy image showed the presence of well-developed pores on the surface of the activated carbon. The presence of important functional groups was shown by the Fourier transform infrared spectroscopy spectrum. The adsorption of methyl orange onto the activated carbon reached 100% after 12 min. Kinetic analysis indicated that the adsorption of methyl orange solution by the activated carbon followed a pseudo-second-order kinetic mechanism [36].

S.Arivoli, et al., studied the removal of Rhodamine B from aqueous solution. A carbon adsorbent prepared from acid activated banana bark carbon [37]. The study was done for various parameters like pH, temperature …etc. The

experimental data were correlated reasonably well with the Langmuir and Freundlich isotherms.

Ridha Lafi, et al., studied adsorption of congo red dye from aqueous solutions by prepared activated carbon with oxygen-containing functional groups and its regeneration. Adsorption experiments were carried out as batch studies at different contact time, pH, and initial dye concentration. The dye adsorption equilibrium was attained after 120 min of contact time. Removal of dye in acidic solutions was better than in basic solutions. The adsorption of dye increased with the increasing of initial dye concentration. The equilibrium data were revealed that Langmuir model was more suitable to describe the congo red adsorption and demonstrated excellent reusability potential with desorption greater than 90% throughout six consecutive adsorption–desorption cycles. Experimental data founded that kinetics followed a pseudo-second-order equation. Thermodynamic study showed that the adsorption was a spontaneous and exothermic process [38].

Syieluing Wong, et al., studied the effective removal of anionic textile dyes using adsorbent synthesized from coffee waste adsorption of Reactive Black 5 and Congo Red from aqueous solution. The removal percentages of both dyes increased with amount of polyethyleneimine in the modified adsorbent. Characterization revealed that polyethyleneimine modification improved the adsorbent surface chemistry, while slight improvement of adsorbent textural properties was also observed. The adsorbent's excellent performance was demonstrated by high removal percentages towards the anionic dyes in most experimental runs. The modelling result showed that anionic dyes adsorption occurred via monolayer adsorption, and chemisorption was the rate-controlling step. The adsorbent possesses higher maximum adsorption capacity towards Reactive Black 5 (77.52 mg/g) than Congo Red

(34.36 mg/g), due to the higher number of functional groups in Reactive Black 5 that interact with the adsorbent. [39]

S.Wang, et al.,showeda comparative study of removal some dyes, including Rhodamine B, from aqueous solution. Fly ash was treated by methods like conventional chemical, sonochemical and microwave [40]. It was found that adsorption capacity of HCl treated fly ash varies with the preparation conditions. The results showed that the microwave treatment was fast and efficient method for producing the sample with the highest adsorption capacity. The experimental data fitted well with the Freundlich and Redlich-Peterson models.

N.M.Mahmoodi, et al., studied the ability of activated carbon in the removal of two anionic dyes (Direct Blue 78 and Direct Red 31) from colored wastewater in single and binary systems [41]. The effects of adsorbent dosage and initial dye concentration were studied at 25℃. The kinetics was found to conform to pseudo second order kinetic model. The equilibrium data fitted well with Langmuir adsorption isotherm. Results indicated that Activated Carbon is an effective adsorbent in this case.

B.Dash, et al., studied competitive adsorption of dyes (congo red, methylene blue, malachite green) on activation carbon [5]. It was found that the percent removal of color increased with the increase in the amount of adsorbent dosage and also with the increase in contact time. It also observe that the adsorption varies with changing the value of pH of dye solution.

N.Kannan, et al., studied the methylene blue adsorption on commercial activated carbon and indigenously prepared activated carbon from bamboo dust, coconut shell, groundnut shell, rice husk and straw[42]. The effects of various experimental parameters were investigated. The experimental data fitted well with the Langmuir and Freundlich adsorption isotherms. The

results also indicated that the indigenous activated carbon can be employed as low cost alternative to the commercial activated carbon.

Ruqia Nazir, et al., studied waste seeds activated carbon which derived from Monotheca buxifolia. Waste seeds were used for the adsorptive removal of a number of selected azo dyes such as Eriochrome Black T (EBT), Remazol brilliant blue (RBB), Remazol yellow (RY) and Remazol brilliant orange (RBO) from an aqueous solution by changing the initial dye concentration, adsorbent dosage, solution pH, contact time and temperature. A Fourier transform infrared spectroscopic analysis of the activated carbon showed the existence of hydroxyls, methyl, methylene, carbonyls, alkane and alkenes groups while the scanning electron microscopic image displayed the gradual formation of cavities and open pores on the surface. The results showed that as the amount of the adsorbent and the shaking time were increased, the removal percentage of the dye increased accordingly. Higher adsorption percentages were observed at a lower dye concentration and temperature in an acidic media. The investigated data were evaluated with the Langmuir and Freundlich adsorption models. The maximum adsorption capacities obtained from the Langmuir model were 112.36, 96.34, 97.65 and 90.91 mg/g for EBT, RBB, RY and RBO, respectively. The results indicated that the electrostatic interaction was the main cause of the adsorption of these anionic azo dyes on the surface of the activated carbon. [43]

Feng, Q., et al., studied the adsorption behavior of a basic dye from aqueous solution onto alkali extracted lignin, Alkali extracted lignin (AEL), isolated from corn stalks with dilute alkali solution under mild condition, was used as a low-cost adsorbent for the removal of methylene blue (MB) from aqueous solutions. Batch adsorption studies were conducted to evaluate various experimental parameters such as pH, contact time, and initial dye concentration for the removal of MB. The kinetic data were analyzed using

pseudo-first-order and pseudo-second-order kinetic models, and the adsorption kinetics were found to be well represented by the pseudo-second-order kinetic model. The equilibrium data were perfectly fitted to the Langmuir isotherm equation when compared with Freundlich isotherm equation. Based on the Langmuir adsorption isotherm model, the predicted maximum monolayer adsorption capacity was found to be 121.20 mg g-1 (at 30 ºC). The results showed that this adsorbent had a high adsorption capacity, making it a promising alternative for dye removal.[44]

1.16- STUDY OBJECTIVES:

1.16.1 General objective

The main objective of this study is to investigate the dye removal efficiency of seaweed from aqueous solution.

1.16.2 Specific objectives

1- In the current study the effort is being done to optimize the use of local Libyan seaweed to remove synthetic dyes(Methylene blue, Crystal violet, Methyl green) from aqueous solution.

2- Some parameters have been investigated and optimized (pH, adsorbent particle size, concentration dyes, temperature, etc.).

3- Determine dye removal efficiency of the adsorbent

4- Fitting the experimental data to theoretical mathematic adsorption isotherms such as Langmuir and Freundlich.

1.16.3 Significance of the study

This study should be significant in the sense that:

- Add to the knowledge of dye adsorption process by seaweed adsorbent.

- Its application in textile wastewater treatment method can be a choice, to reduce the impact of dyes colored wastewater on the environment.

- Improve the value such a material are important for the economy of the countries by reducing cost of solid waste management.

MATERIALS AND METHODS

2.1 Chemicals and Materials:

All chemicals which were used in this study were of analytical reagent grade.

-1000 ppm of standard stock solutions from Methylene Blue, (Northampton, UK)

- 1000 ppm of standard stock solutions from Crystal Violet, (Northampton, UK)

-1000 ppm of standard stock solutions from Methyl Green, (BDH) chemical, France

Hydrochloric acid HCL (36%) (Eurostar scientic limited, UK)

Sodium hydroxide, NaOH (Midleks Est., Geneve, UK)

$(Na_3PO_4, BaCl_2, Na_2SO_4, NaCl, Na_2CO_3)$,(Eurostar scientic limited, UK)

2.2-Instrumentation:

Table (2.1) list of all instruments used in this study:

Order	Instruments	Company name
1	Electronic weight balance	Switzerland, 1000±0.0001g
2	PH meter	WTW525, Germany
3	Spectrophotometer(UV/Vis)	Shelton, CT 06484 USA
4	Shaker	SWB20, Germany
5	Sieve	Tronic 24048, Italy
6	Oven	Shivaki, Germany
7	Scanning Electron Microscope (SEM)	Shivaki, Germany
8	FT-IR	Shivaki, Germany
9	Centrifuge	Z 300, Germany

2.3- Procedures:

2.3.1- Preparation of Adsorbent:

The dead leaves of seaweed were collected from the coast of Subrata in January 2017 (Fig. 2.1). The material was first washed with tap water to remove salt, and then was washed with distilled water. The material was dried at 100°C for 24 h [60]. The dried material was grinded by a mortar that was sieved by a sieve and the particle size obtained was 100, 150 and 300 micron. A 100 micron was used in these experiments. as shown in Figure (2.2).

Figure (2.1) dead leaves of seaweed were collected from coast Subrata.
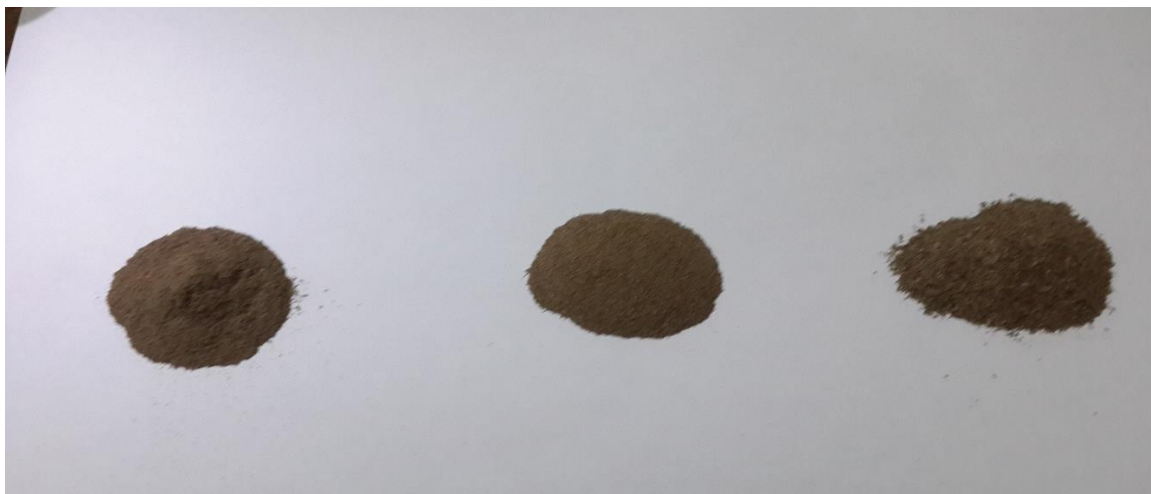
100 micron   150 micron   300 micron of seaweed

Figure (2.2) Ground dead leaves of seaweed.

2.3.2- Preparation of Stock Solution:

Stock solution of MB was prepared by dissolving 1g of MB in one liter of distilled water to yield a stock solution of 1000mg/L MB. The MB standard solution were prepared by diluting this stock solution to the desired concentration. The same procedures for preparing standard solution were followed for the other two dyes (CV, MG) solution. Then solutions of (2.5, 5, 10, 20, 40, 80) ppm were prepared.

2.3.3-Prepration of mixture salt:

Mixture salt of (Na_3PO_4,$BaCl_2$,Na_2SO_4,$NaCl$,Na_2CO_3) was prepared by dissolving 0.1g from all types of salt in 1000 ml distilled water to yield a mixture salts of 100 ppm.

2.4 The effect of variable parameters:

2.4.1- The effect of dye concentrated on seaweed:

To determine the dye removal values on seaweed surface, 0.15g of seaweed was placed in a glass flask containing 50 ml of dye concentrated (2.5mg / L) of dye. The mixture was mixed with the SWM20 shaked for 3 hours and placed in a centrifuge for 12 minutes. Remaining dye concentrations in supernatants were analyzed at (663, 590 and 631.85) nm of MB, CV and MG respectively in UV-VIS Shelton, CT 06484 Spectrophotometer. The optical absorption value of the pure dye solution is determined before and after mixing. All the experiments were assayed in triplicate. The same steps were followed at the following dye concentrations, (5, 10, 20, 40, 80) mg / L

2.4.2- The effect of Contact time on dye removal:

In this experiment the same steps were followed as in paragraph (2.4.1) However, the absorption values of the sample were measured after 5, 10, 30, 60, 90, 120, 150 and 180 minutes, respectively. The pH of solution was 3, at

concentration 10 ppm of MB, CV and MG, 0.15g of seaweed and the solution temperature was 25℃.

2.4.3- The effect of mass of adsorbent (dose) on dye removal:

A sample weighted were obtained in 0.05, 0.1, 0.15, 0.2, 0.25, and 0.3 g of seaweed were measured. And the removal process was as in the steps mentioned in paragraph (2.4.1). The pH of solution was 3 the temperature of solution was 25℃ and the time was 180 minutes.

2.4.4-The effect of pH on dye removal:

The removal of dyes from aqueous solutions by adsorption is affected by controlling the pH of the solution, since pH affects the surface charge of the adsorbents and degree of ionization. Keeping all other parameters constants, pH of solution was varied from 2 to 9 by addition of 0.1N HCL and 0.1N NaOH. At concentration 10 ppm of MB, CV and MG, 0.15g of seaweed, the solution temperature was 25℃ and the time was 180 minutes.

2.4.5-The effect of temperature on dye removal:

The same steps as above were followed to measure the temperature of the removal except that the temperature has been raised to the following temperatures 20, 30, 40, 50 using a water bath. At the pH of solution 3, 0.15g of seaweed and the reaction time 180 minutes.

2.4.6- The effect of particle size on dye removal:

To test the effect of particle size on removing the dyes were investigated by using various particle sizes of the adsorbent (100, 150 and 300 micron). At the reaction time is 180 minutes, pH 3 and 0.15g of seaweed.

2.4.7- The effect of foreign ions on dye removal:

The effect of foreign ions on the removal of the dye was measured by the same steps as in paragraph (2.4.1) at the following times from 5 to 180 minutes with the addition 50 ml of 100 ppm of foreign ions

(Na_3PO_4, $BaCl_2$, Na_2SO_4, NaCl, Na_2CO_3). At concentration 10 ppm of MB, CV and MG, 0.15g of seaweed, the solution temperature was 25℃, and the pH of dye solution was 3.

2.4.8-The effect of photolysis on the dye:

In this experiment, a 100-volt light bulb was placed at a distance of 20cm on the mixture containing dye and seaweed and tracked the changes in the mixture with a time tracking of 5 to 120 minutes. At concentration of 10 ppm of solution, 0.15g of seaweed, the solution temperature was 25℃ and the pH of dye solution was 3.

RESULTES AND DISCUSSION:

This chapter provides result of laboratory analysis made for seaweed preparation and discusses some factors affecting dye adsorption such as initial solution pH, adsorbent dose, initial dye concentration and contact time by seaweed adsorbent from aqueous solution and findings of other scientific data generated from this study.

3.1-FTIR characterization of the seaweed:

FTIR spectroscopy offers excellent information on the nature of the bonds found on the surface of seaweed. Several intense characteristic bands in the IR spectra can be attributed to functional groups found in seaweed. The results are shown in Table (3.1). The peaks obtained from grinded seaweed attributed to functional groups are at: 3420 (–OH, NH_2), 2920 (–COOH, Alkyl (C-H), 2550 (S–H), 1053 (C-O) and 1629 (C=O), 1265 (S=O), 619 (S–O) cm^{-1}. The IR spectra of seaweed with adsorbed Methyl Green showed a disappearance of the extension shown in the range (2550) cm^{-1} to the S-H groups in the IR stretch of functional group compared to pure seaweed in the figure. (3.4). While when Methylene Blue, Crystal Violet was adsorbed onto seaweed certain functional group (S-H) shows a greater shift in IR. From these findings it is presumed that the dye is incorporated within the adsorbent through interaction with the active functional groups or this indicates the occurrence of chemical adsorption. in the figure. (3.2) and (3.3).

Table (3.1). Functional groups of dried seaweed with adsorbed MB, CV and MG and their corresponding wavenumber in cm^{-1}.

Functional group	Standard wavenumber[45]	Wavenumber seaweed
Hydroxyl -OH	3250–3700	3420
Amine -NH_2	3300–3500	3420
Carboxyl -COOH	2400–3000	2920
Thiol -S–H	2550-2600	2550
Carbonyl C=O	1550-1750	1629
C–O	1050–1300	1053
Alkyl: CH	2900-3000	2920
Sulfonyl S=O	1040-1200	1265
S–O	550-650	619

3.1.1- FTIR spectra for seaweed before and after addition of Methylene Blue Crystal Violet and Methyl Green:
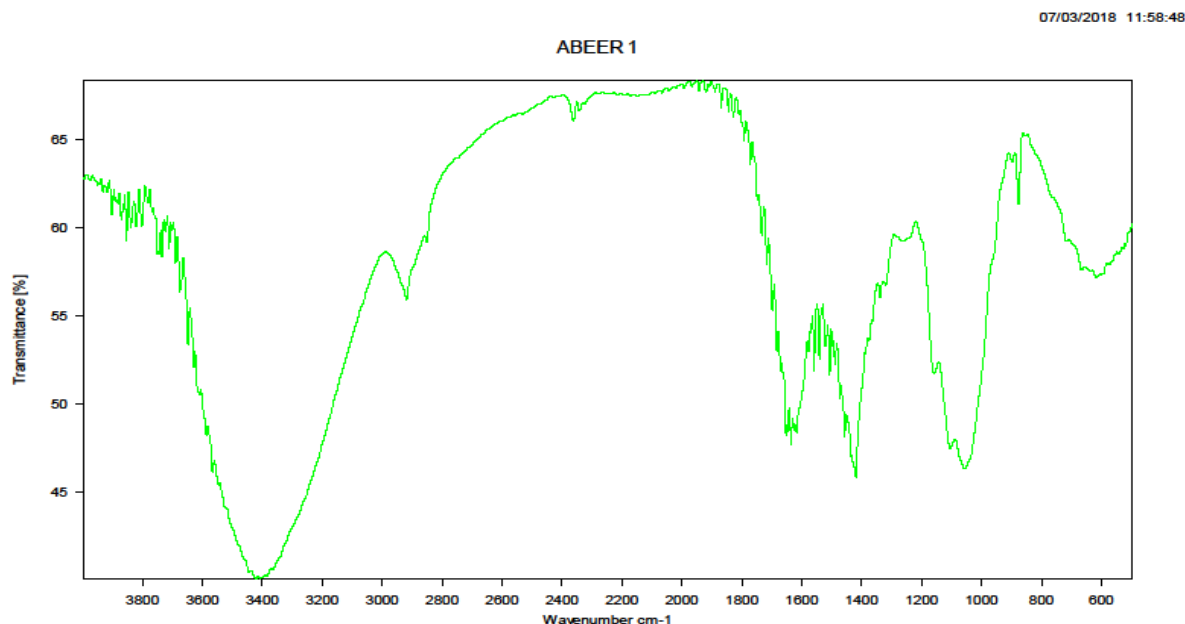
Figure (3.1) FTIR spectra for Seaweed before addition of dye.
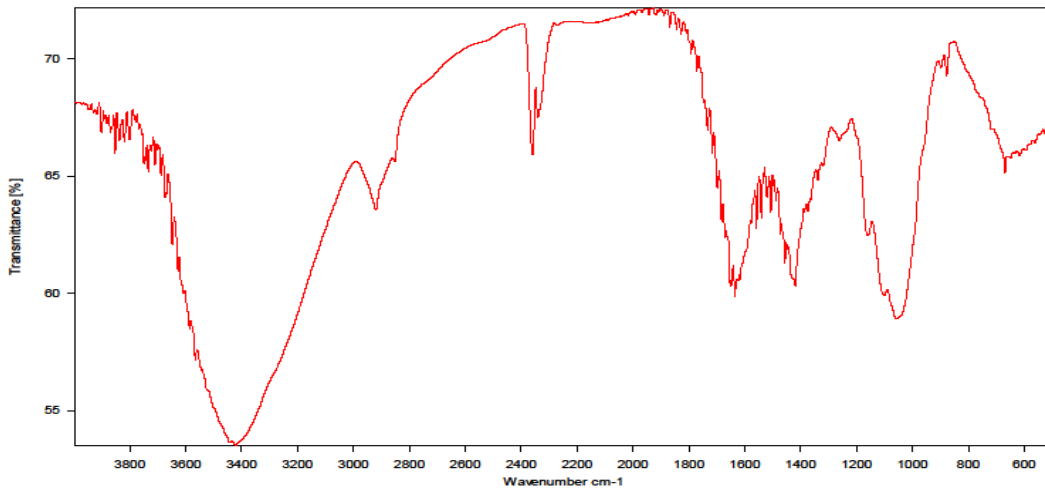
Figure (3.2) FTIR spectra for Seaweed after addition of MB.
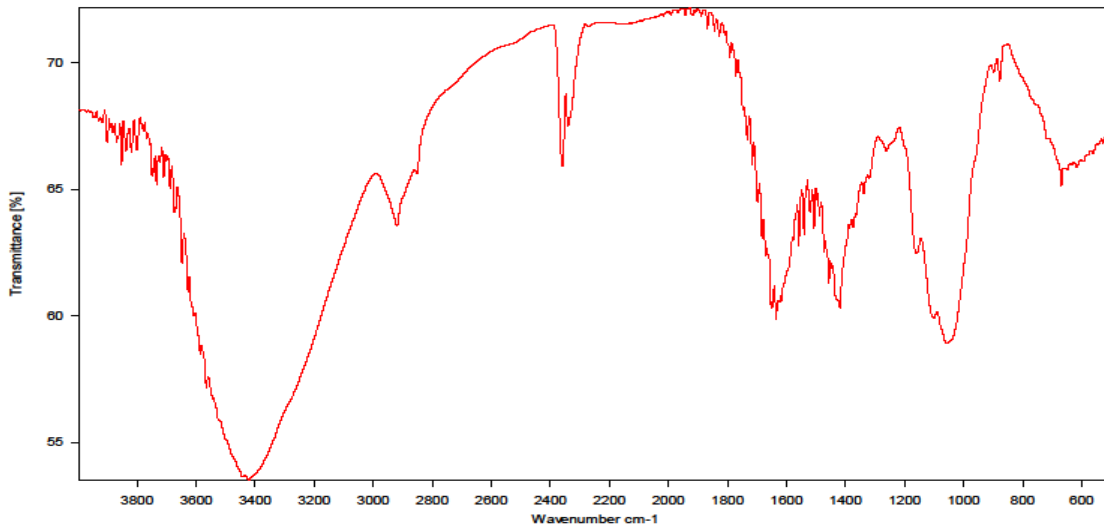
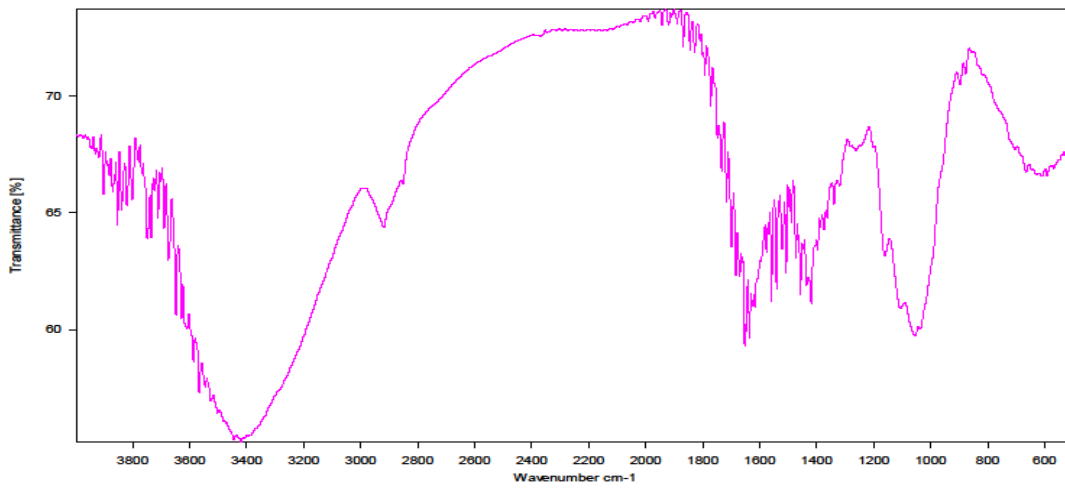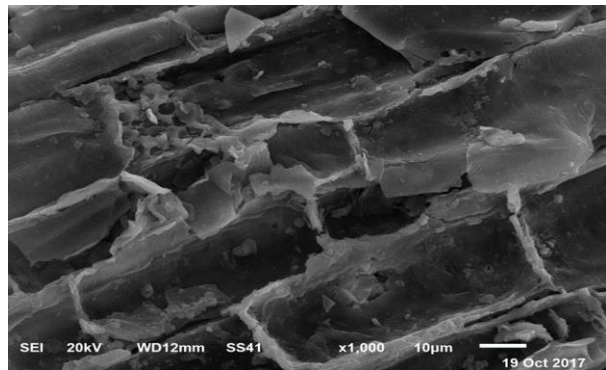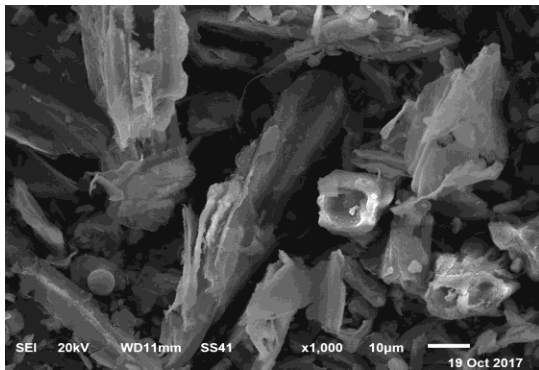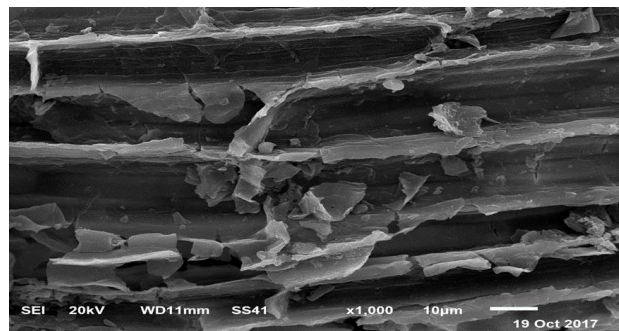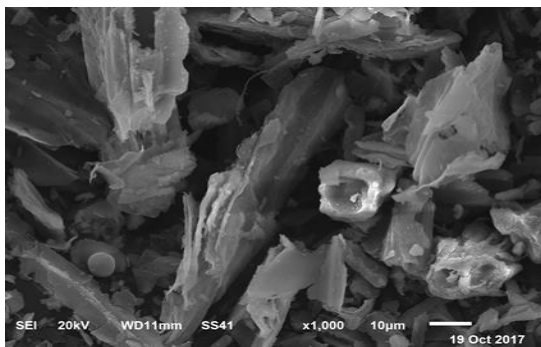Figure (3.3) FTIR spectra for Seaweed after addition of CV.

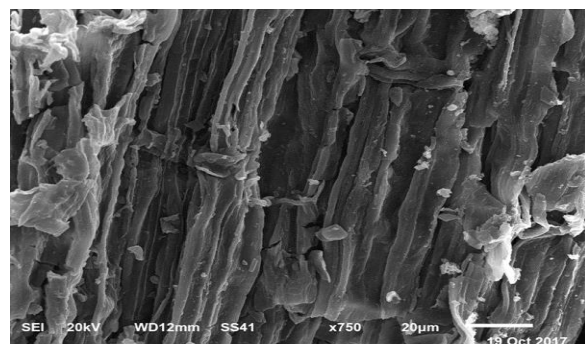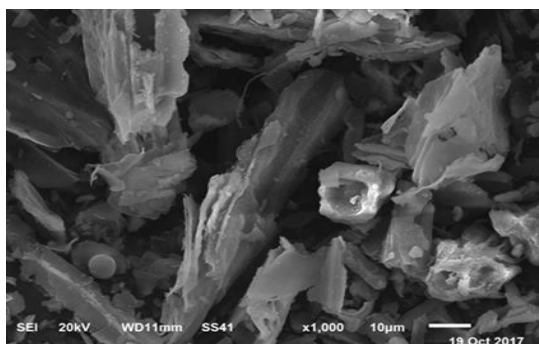Figure (3.4) FTIR spectra for Seaweed after addition of MG

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3.2.Scanning Electron Microscope SEM of the seaweed and dyes:

a) SEM for seaweed before addition of dye   b)- SEM for seaweed after addition of Methylene blue dye

a) -SEM for seaweed before addition of dye   c) - SEM for seaweed after addition of Crystal violet dye.

a) -SEM for seaweed before addition of dye   d) - SEM for seaweed after addition of Methyl Green dye.

Figure (3.5). Scanning electron microscopy of the surface of seaweed before (a) and after (b, c, d) MB, CV, MG dye treatment.

SEM gives us images of the sample surface through the scan that gives it the electron beam emitted from it. This beam interacts with the atoms in the sample to give an image of the shape and topography of the sample. An assessment of the morphological changes in seaweed in response to dye adsorption was performed by SEM (Figure 3.5). The seaweed were smooth with a highly porous structure that was hole-like before exposure to MB, CV and MG dye (Figure 3.5 a). After exposure of the seaweed to the dye ions, the surface became rough and meandrous due to precipitation of dye ions around the seaweed surface (Figure 3.5, b, c and d).[29]

3.3- (UV/Vis) Spectrophotometer Results for MB, CV and MG:

Fig.(3.6) (UV/Vis) for MB before add seaweed   (UV/Vis) for MB after adding of seaweed. At 10 ppm from MB, 3h, pH = 3, 0.15g of seaweed.
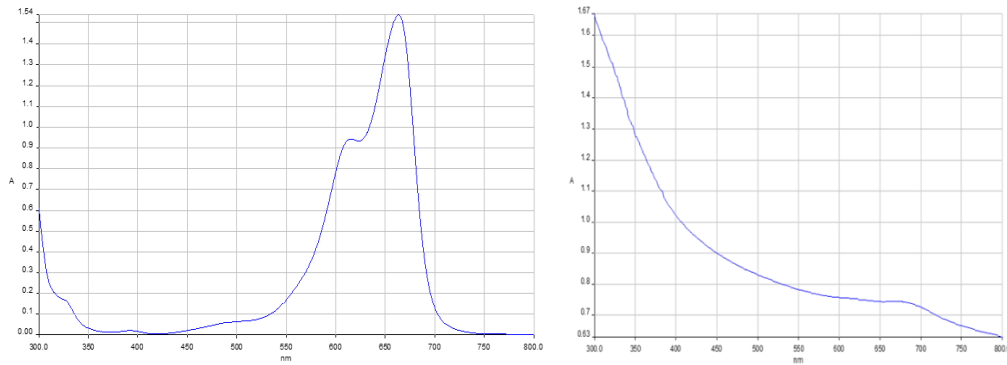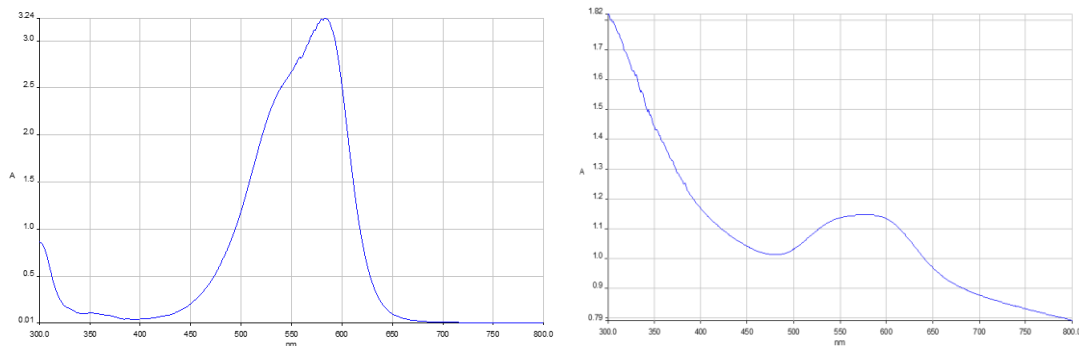

Fig.(3.7)(UV/Vis) for CV before add seaweed   (UV/Vis) for CV after adding of seaweed. At 10 ppm from CV, 3h, pH = 3, 0.15g of seaweed.
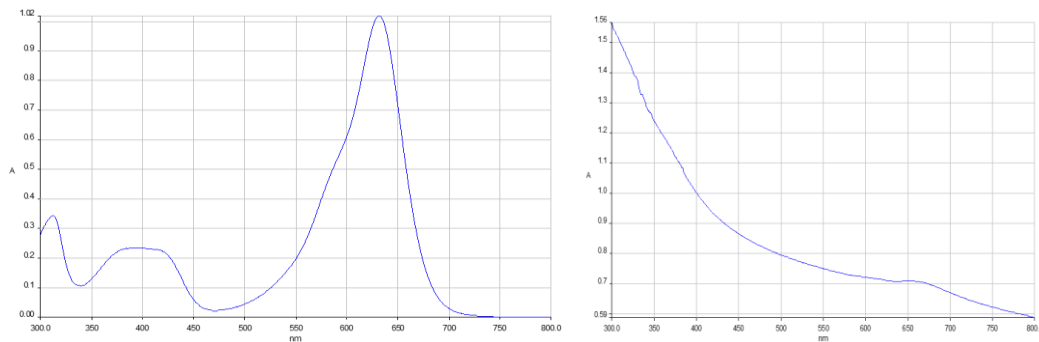
Fig.(3.8) (UV/Vis) for MG before add seaweed   (UV/Vis) for MG after adding of seaweed. At 10 ppm from MG, 3h, pH = 3, 0.15g of seaweed.

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Through the results obtained using a spectrophotometer, we notice that when measuring the adsorption of the dye before the adsorption process, the obtained peak was high, as this peak disappeared after the adsorption process, as shown in the figure ((3.6) (3.7) (3.8)) of the dye (MB, CV and MG) respectively which indicates that the seaweed has a high adsorption capacity.

3.4 Results of removal methylene blue, crystal violet, methyl green on the seaweed:

3.4.1- Results of removal of methylene blue on the seaweed:

The ability of seaweed to adsorb methylene blue from aqueous solutions was studied by observing the change in the rate of dye removal on the seaweed surface. This was by following the change in the absorption value of the solutions before and after the addition of seaweed and under the influence of the following factors: time, weight of seaweed, initial concentration of dye, temperature, light, particle size of seaweed, effect foreign ions and pH. The optical absorption of samples was measured at the maximum absorption wavelength (663.8 nm) and the concentration of the dye solution (2.5, 5, 10, 20,40, 80 ppm). Figure (3.9) illustrates the spectral curve and the standard curve of the methylene blue dye solutions.
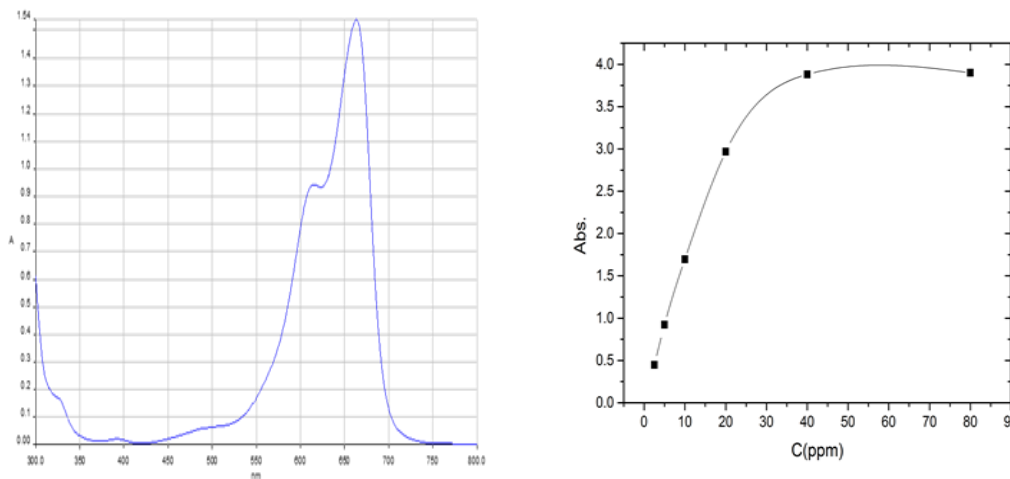

Figure (3.9) UV-VIS spectrum and Calibration curve of MB dye. At 0.15g of seaweed, pH 3, 3h, 25°C .

3.4.2-The effect of Contact Time of methylene blue on seaweed:

Testing the time is one of the basic elements for the study of adsorption properties. It determines the equilibrium time and the saturation point of the

adsorbent material. The amount of dyes adsorbed on seaweed increased with the increasing reaction time. Figure (3.10) show the effect of contact time on MB removal. The amount of dye removal increased with increasing the time indicating that the seaweed surface saturation points of the dye. The highest clearance was on seaweed surface (94.79%) after 3h. at 25°C, pH 3, the concentration of solution 10 ppm and the mass of 0.15 g. The equation (3-1) describes the value of removal as

$$\% \ \mathrm{Removal} = \frac{C_o - C_e}{C_0} \times 100 \qquad \dots (3\text{-}1)$$

C_o Initial concentration, C_e dye concentration at time t.

Table (3.2) the effect of Contact time on MB removal. At 10 ppm, 0.15 g of seaweed, pH 3, 25°C.

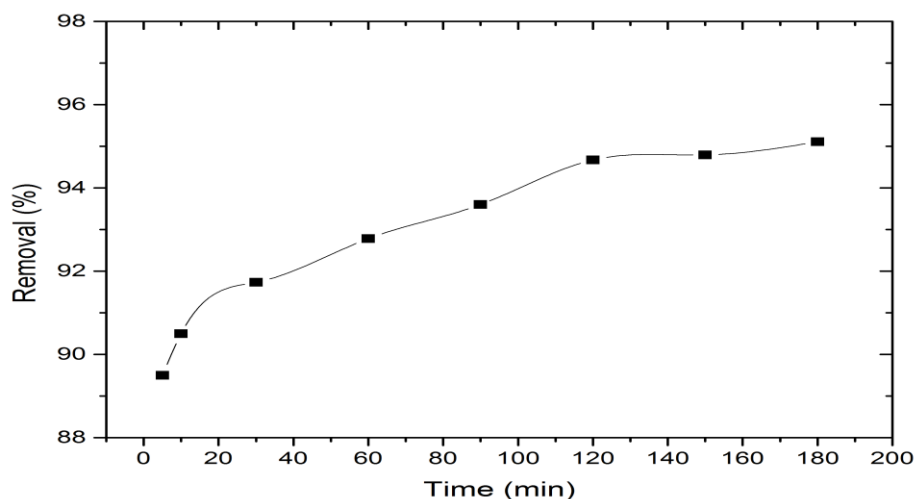| Contact Time C_o (min.)	Average C_e (ppm)	Percentage removal (%)
5	1.049	89.50
10	0.975	90.50
30	0.803	91.73
60	0.721	92.78
90	0.639	93.60
120	0.520	94.67
150	0.532	94.79
180	0.532	94.79

Figure (3.10) The effect of Contact time on MB removal. At 10 ppm, 0.15 g of seaweed, pH 3, 25°C .

3.4.3-The effect of Initial pH:

The removal of dye from aqueous solution by adsorption is related to the pH of the solution, since pH affects the surface charge of the adsorbent and also the degree of ionization. Keeping all other parameters constant, at concentration for dyes 10ppm, 180 minutes, and 0.15g for seaweed, and pH of solution was varied from 2 to 9 by addition of 0.1N HCL and 0.1N NaOH.

3.4.3.1- The effect of Initial pH:

Figure (3.11) shows the effect pH on MB removal. The adsorption density of MB onto seaweed increased from pH 2 to 3, and decreased slightly from pH 4 to 9. The decrease in three dyes adsorbed from (4-9) is probably because the removal of the dye is more favorable due to the presence of carbonyl and hydroxyl functional groups on the surface on the adsorbent. In acidic condition, the functional groups of the adsorbent surface polarize. Thereby creating electrostatic interaction alongside with hydrogen bonding and van der walls interaction.

Table (3.3) the effect of pH on MB removal. At 10 ppm, 0.15g of seaweed, 3h, 25°C

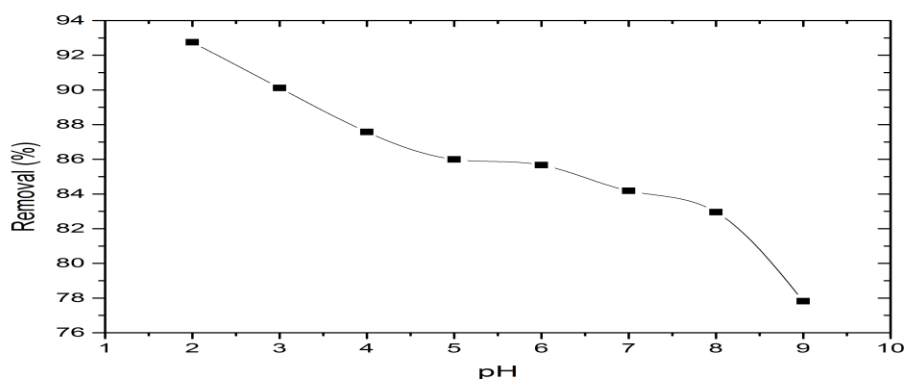| pH	Average C_e (ppm)	Percentage removal (%)
2	0.724	92.75
3	0.125	90.11
4	1.244	87.58
5	1.400	85.99
6	1.432	85.67
7	1.581	84.18
8	1.708	82.95
9	2.2172	77.82

Figure (3.11) The effect of pH on MB removal. At 10 ppm, 0.15g of seaweed, 3h, 25°C

3.4.4-The effect of Initial Dye Concentration:

The effect of initial dye concentration on the rate of adsorption by seaweed was carried out at pH 3, with 0.15g of seaweed. The initial concentration values were prepared by diluting a known value from stock standard solution to 50ml volumetric flask with distilled water to prepare (2.5, 5, 10, 20, 40, 80 ppm). Studying of the effect of initial dye concentration on the rate of adsorption by seaweed was revealed that maximum dye removal is obtained with lower dye concentration shown in figure (3.12). The results show that 10 ppm is the optimum concentration. This observation can be

explained by the fact that at a very low concentration of dye, the ratio of adsorption surface area to the total dye available is high, this is a greater chance for dye removal. Thus, at low initial dye concentration, the removal capacity is higher. When dye is increased, binding sites become more quickly saturated as the amount of biomass remained constant.

Table (3.4) the effect of initial dye concentration on MB removal. At 0.15g of seaweed, pH 3, 3h, 25°C.

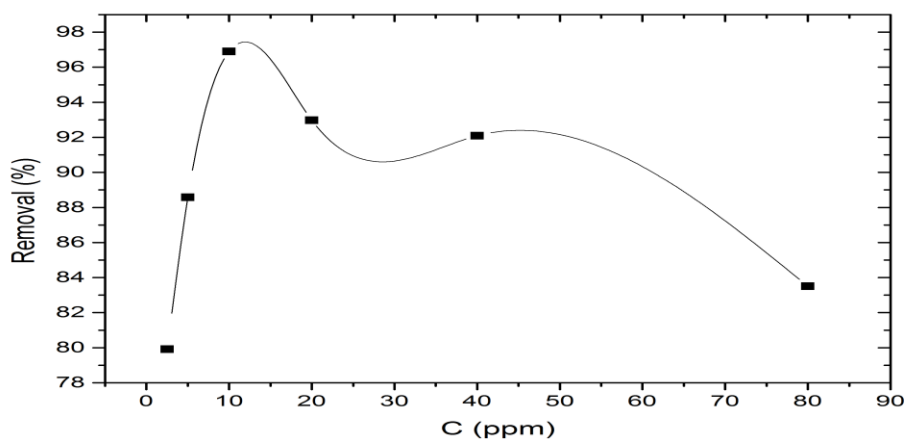| Concentration (ppm)	Average C_e (ppm)	Percentage removal (%)
2.5	0.501	79.92
5	0.571	88.58
10	0.309	96.90
20	1.405	92.97
40	2.942	92.09
80	13.189	83.51

Figure (3.12) the effect of initial dye concentration on MB removal. At 0.15g of seaweed, pH 3, 3h, 25°C

3.4.5- The effect of mass of adsorbent (dose):

The amount of material adsorbed on the surface of the adsorbate is estimated by the Q value shown in equation (3.2). Figure (3.13) shows the

relationship between mass of adsorbent with the amount of removal Q. The increase in seaweed mass increases the amount of dye removal. As one was expected, the percentage of dye removal increased with increasing the amount of seaweed. However the ratio of dye adsorbed to seaweed (mg g-1) decreased with the increasing amount of seaweed. The ratio of dye adsorbent to seaweed was started to reach equilibrium at 0.15g seaweed. (94.72%) with pH 3 and temperature 25 ° C and time was 3h. The absorbance of all the solutions was then measured. A graph was plotted with percent removal (% Q) vs. adsorbent dose.

The equation used for calculating equilibrium capacity is:

$$q_{e=}\frac{(C_0-C_e)}{m}V \qquad \qquad \dots (3.2)$$

$q_{e=}$ The adsorption density mg of adsorbate per g of adsorbent.

C_0 = The concentration of adsorbate in solution mg/L.

C_e = Final equilibrium concentration of adsorbate after adsorption has occurred, mg/L. V= Volume of liquid in the reactor, (L), m = mass of adsorbent, (g).

Table (3.5)the effect of adsorbent dose on MB removal. At 10 ppm, pH 3, 3h, 25°C.

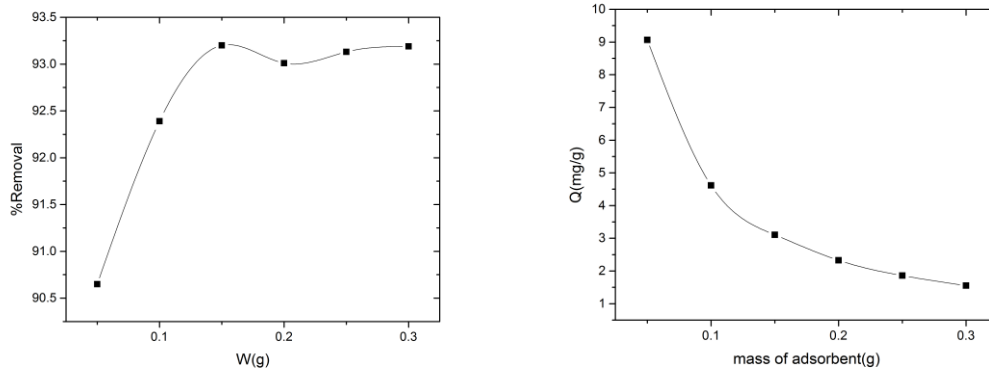| Weight(g)	Average C_e (ppm)	Percentage removal (%)
0.05	0.935	90.65
0.1	0.761	92.39
0.15	0.679	93.25
0.2	0.698	93.01
0.25	0.686	93.13
0.3	0.674	93.19

Figure (3.13)the effect of adsorbent dose on MB removal. At 10 ppm, pH 3, 3h, 25°C

3.4.6- The effect of particle sizes:

The removal of MB at these different particle sizes showed that the capacity of MB adsorption at equilibrium increased with the decrease in particle size. The relatively higher adsorption with smaller adsorbent particle may be attributed to the fact that smaller particles yield large surface areas and indicating the MB adsorption occurs through surface mechanism. The effect of particle size on MB removal at 100, 150 and 300-micron particle sizes is shown in Figure (3.14).

Table (3.6)the effect of particle size on MB removal. At 10 ppm, pH 3, 3h, 25°C.

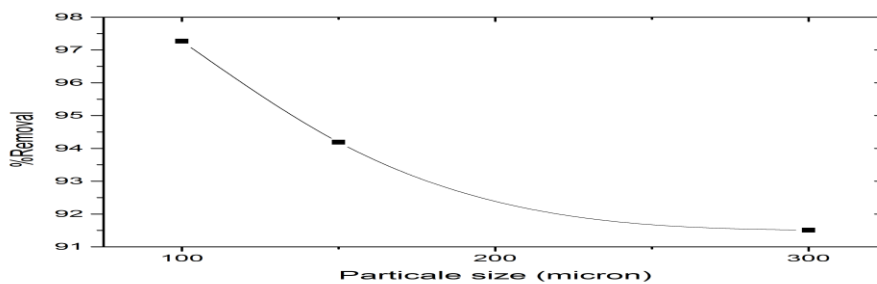| Particle Size (micron)	Average C_e (ppm)	Percentage removal (%)
100	0.272	97.27
150	0.587	94.13
300	0.843	91.57

Figure (3.14) effect particle size on MB removal. At 10 ppm, 0.15g, pH 3, 3h, 25°C

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3.4.7-The effect of Temperature on removal of methylene blue:

Results indicate that the adsorption capacity of seaweed for MB decreased with increasing temperature. This is because experimental results show that the amount of dye adsorption on the surface of seaweed decreases with increasing temperature. The adsorption process this is in line with the thermodynamic requirements of the adsorption process. The heat increases the kinetic energy of the adsorbed molecules on the surface of the adsorbent, which in turn increases the likelihood of their separation the surface of the adsorbent and its return in the solution. The effect of temperature of on MB removal is shown in Figure (3.15).

Table (3.7) the effect of temperature on MB removal. At 10 ppm, pH 3, 3h, 0.15g.

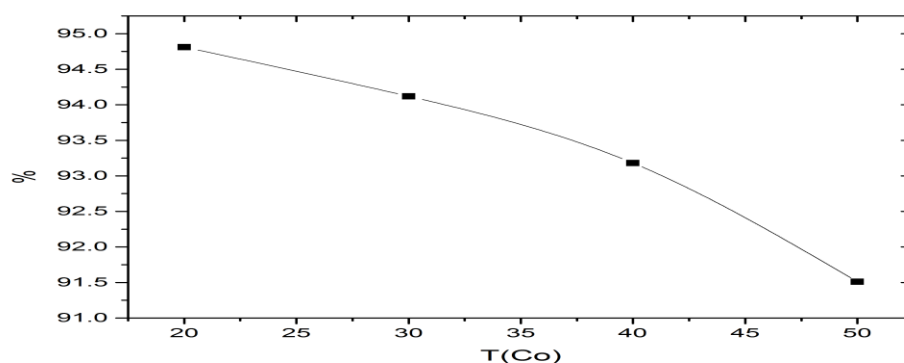| Temperature($^{\circ}$C)	Average C_e (ppm)	Percentage removal (%)
20	0.843	94.81
30	0.681	94.12
40	0.587	93.18
50	0.518	91.56

Figure (3.15) the effect of temperature on MB removal. At 10 ppm, pH 3, 3h, 0.15g.

3.4.8- The effect photolysis:

Photolysis of the dye was observed on the seaweed surface by tracking the change of solutions over time and under the light of a 100-watt lamp at a

distance of 20cm. In Figure (3.16) the resulting values increase with the removal time during the first half an hour. The removal rate then decreases over time, indicating a gradual change in the electronic or chemical composition of the dye under mixture conditions.

Table (3.8) effect photolysis on MB removal. At 10 ppm, pH 3, 0.15g, 25°C.

Time(min.)	Average C_e (ppm)	Percentage removal (%)
8	0.943	92.69
10	0956	92.85
12	0.951	93.02
14	0.912	93.34
16	0.896	93.75
30	0.679	95.38
60	0.873	94.61
120	0.969	91.3
180	1.151	89.83

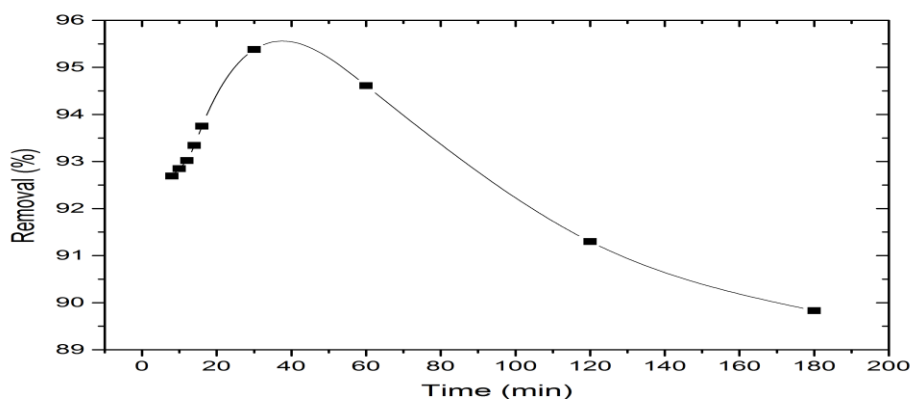Figure (3.16) effect photolysis on MB removal. At 10 ppm, pH 3, 0.15g, 25°C

3.4.9- The effect of foreign ions:

The effect of adding ions to removal of the dye for a predetermined time period ranging from 5-120 minutes with adding 50ml from 100ppm from mixture ions ($Na_3PO_4, BaCl_2, Na_2SO_4, NaCl, Na_2CO_3$) to 50ml from MB. pH is 3 and the mass of the seaweed is 0.15 g. The removal of dye on the surface

of the seaweed when the ions were added increased with time. Figure (3.17) shows a gradual change in the chemical composition of the dye.

Table (3.9) the effect of foreign ions on MB removal. At 10 ppm, pH 3, 0.15g, 25°C

Time(min.)	Average C_e (ppm)	Percentage removal (%)
5	1.371	86.28
10	1.306	86.93
30	1.306	86.93
60	1.208	87.91
90	1.183	88.16
120	1.134	88.65
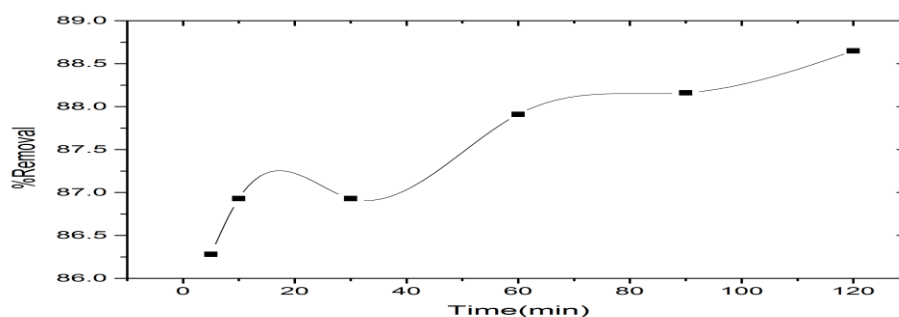
Figure (3.17) the effect of foreign ions on MB removal. At 10 ppm, pH 3, 0.15g, 25°C

3.5- Results of Removal of Crystal violet on the seaweed:

The ability of seaweed to adsorb crystal violet from water solutions was studied in the same manner as for the measurement of methylene blue. The optical absorption of dye solutions was measured at the maximum absorption wavelength (580nm) by Shelton spectrophotometer (UV/Vis) and the primary concentration of the dye solution (10ppm) pH 3, 0.15g and 3h. (Fig. 3.18) shows the UV-VIS spectrum and Calibration curve of CV dye.
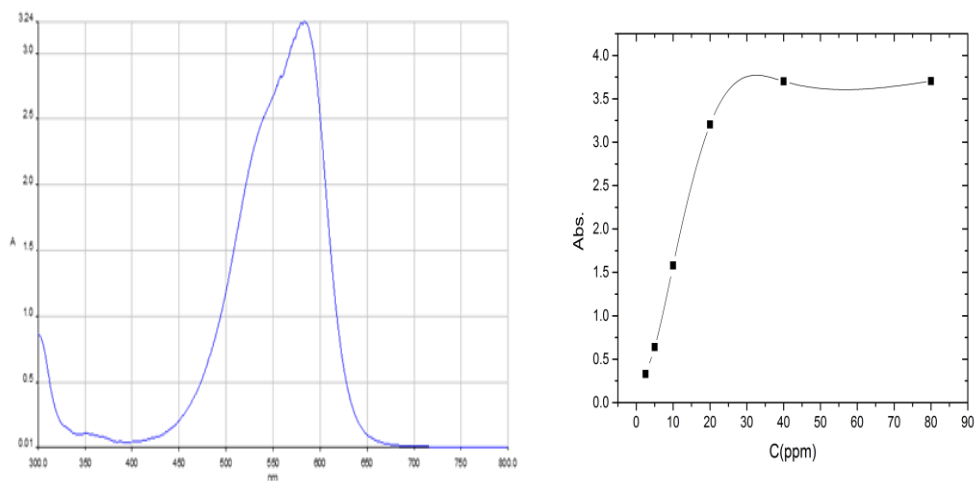
Figure (3.18). UV-VIS spectrum and Calibration curve of CV dye. At 0.15g of seaweed, pH 3, 3h, 25°C

3.6- Results of removal of methyl green on the seaweed:

The ability of seaweed to adsorb of methyl green from water solutions was also studied in the same manner as the two previous dyes. The optical absorption of pigment solutions was measured at the maximum absorption wavelength (631.85nm) and the primary concentration of the dye solution (10ppm), pH 3, 0.15g of seaweed and 3h. The values of CV removal were higher than MB, MG, reflecting the difference in the chemical composition of the dyes and the intertwining forces of the molecules. Figure (3.19) shows the UV-VIS spectrum and Calibration curve of MG dye.
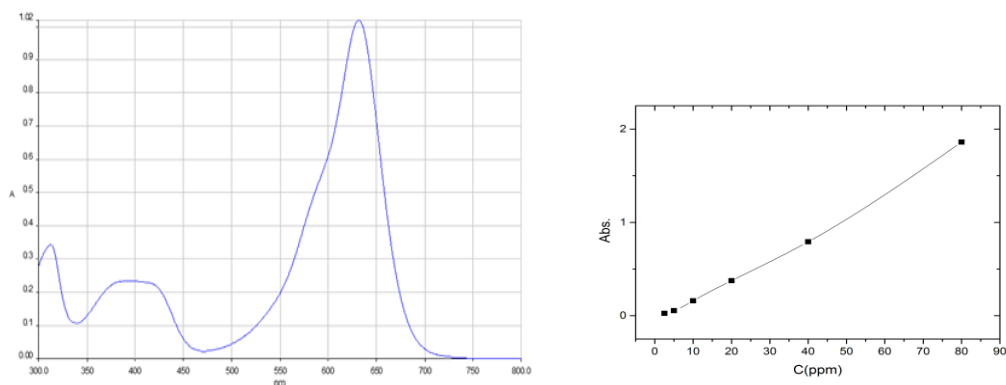

Figure (3.19). UV-VIS spectrum and Calibration curve of MG dye. At 0.15g of seaweed, pH 3, 3h, 25°C

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3.7-Comparing the results of removing methylene blue, crystal violet and methyl green on seaweed:

3.7.1-The effect of Contact Time of methylene blue, crystal violet and methyl green on seaweed:

From the results of the effect of contact time on the removal of MB, CV and MG dye, found that the highest percentage of removal for MB. The removal rate was (94.79%, 90.95% and 94.55%) respectively. figure (3.20) shows the effect of contact time of (MB, CV and MG) on seaweed.

Table (3.10) the effect of Contact time on MB,CV and MG removal. At 10 ppm, 0.15 g of seaweed, pH 3, 25°C.

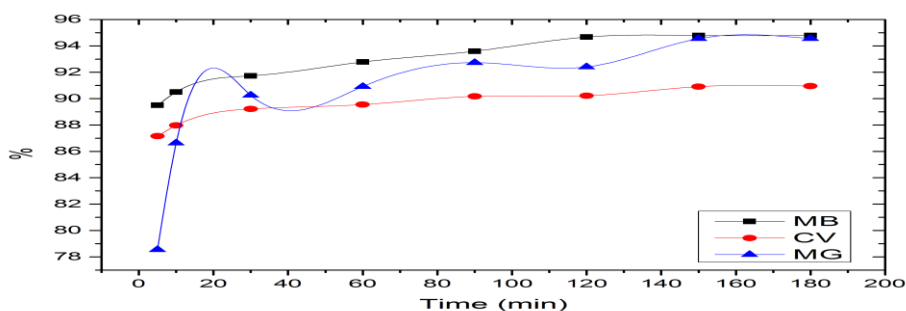| Contact Time(min.)	Average C_e (ppm)			Percentage removal (%)		
	MB	CV	MG	MB	CV	MG
5	1.049	1.283	4.290	89.50	87.16	78.54
10	0.975	1.202	2.67	90.50	87.97	86.63
30	0.803	1.077	1.947	91.73	89.22	90.26
60	0.721	1.044	1.815	92.78	89.55	90.92
90	0.639	0.981	1.452	93.60	90.18	92.73
120	0.520	0.977	1.518	94.67	90.22	92.4
150	0.532	0.908	1.089	94.79	90.91	94.55
180	0.532	0.904	1.089	94.79	90.95	94.55

Figure (3.20) the effect of Contact Time of (MB, CV and MG) on seaweed. At 10 ppm, 0.15g of seaweed, pH 3, 25°C.

3.7.2-The effect of Initial pH on removal of methylene blue, crystal violet and methyl green:

By comparing the effect of pH of the MB, CV and MG removal rate, the highest removal value was observed when the acidity medium was increased and the removal value at pH 2 was (92.75%,91.37%, and 92.02%) respectively. The removal rate is low in the base medium and the removal value at pH 9 was (77.82%,72.26%, and 57.43%) respectively. Figure (3.21) shows the effect of initial pH on (MB, CV and MG) removal.

Table (3.11) the effect of pH on MB,CV, and MG removal. At 10 ppm, 0.15g of seaweed, 3h, 25°C

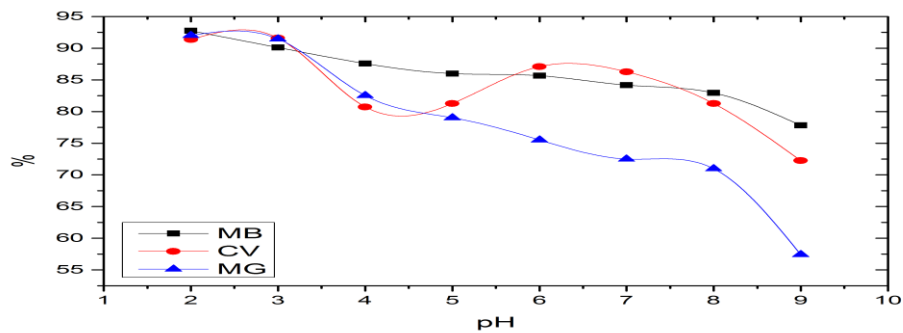| pH	Average C_e (ppm)			Percentage removal (%)		
	MB	CV	MG	MB	CV	MG
2	0.724	0.862	1.595	92.75	91.37	92.02
3	0.125	0.839	1.704	90.11	91.6	91.47
4	1.244	1.926	3.495	87.58	80.73	82.52
5	1.400	1.873	4.193	85.99	81.27	79.03
6	1.432	1.289	4.895	85.67	87.1	75.52
7	1.581	1.372	5.497	84.18	86.28	72.51
8	1.708	0.862	5.802	82.95	91.37	70.98
9	2.217	0.839	8.512	77.82	91.6	57.43

Figure (3.21) the effect of Initial pH on removal of (MB, CV and MG). At 10 ppm, 0.15g of seaweed, 3h, 25°C.

3.7.3- The effect of Initial Dye Concentration on removal of methylene blue, crystal violet and methyl green:

As noticed in the results of the effect of concentration on the removal of MB, MG and CV dyes, the MB dye gave the highest percentage of removal at (10, 20 and 40ppm concentration (96.9%, 92.6%, 80.62%) MB, CV, and MG respectively. In Figure (3.22)shows the effect of Initial Concentration on MB, MG and CV Removal.

Table (3.12) the effect of initial dye concentration on dyes removal. At 0.15g of seaweed, pH 3, 3h, 25°C.

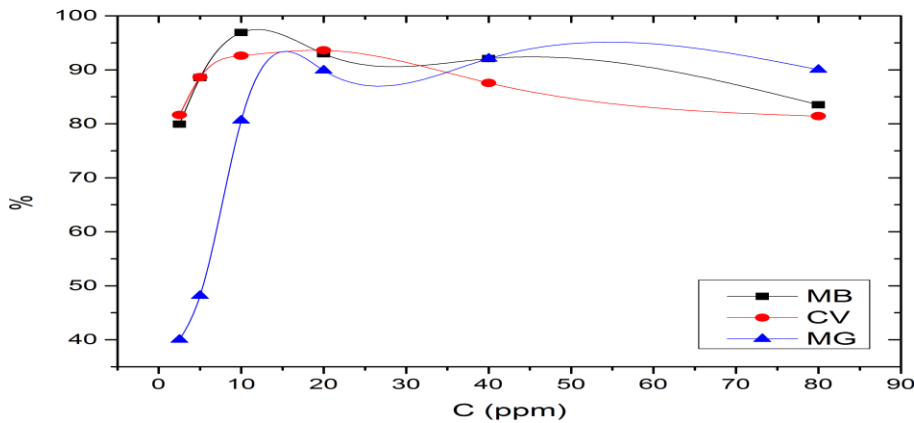| Concentration (ppm)	Average C_e (ppm)			Percentage removal (%)		
	MB	CV	MG	MB	CV	MG
2.5	0.501	0.458	1.5	79.92	81.64	40
5	0.571	0.568	2.59	88.58	88.62	48.14
10	0.309	0.739	1.937	96.90	92.6	80.62
20	1.405	1.278	2.021	92.97	93.6	89.89
40	2.942	4.973	3.171	92.09	87.56	92.07
80	13.189	14.864	7.975	83.51	81.41	90.03

Figure (3.22)the effect of Initial Concentration on removal MB, MG and CV. At 0.15g of seaweed, 3h, pH 3 and 25°C.

3.7.4-The effect of mass of adsorbent (dose) on removal of methylene blue, crystal violet and methyl green :

From the results of the effect adsorbent dose on the removal of MB, CV and MG dyes, note that the MB and CV dye gave the highest percentage of removal at 0.15g (93.25%,94.33%) respectively. MG dye gave the highest percentage of removal at 0.25g (90.48%). Figure (3.23)shows the effect of adsorbent dose on MB, MG and CV Removal.

Table (3.13)the effect of adsorbent dose on dyes removal. At 10 ppm, pH 3, 3h, 25°C

Weight(g)	Average C_e (ppm)			Percentage removal (%)		
	MB	CV	MG	MB	CV	MG
0.05	0.935	0.916	2.178	90.65	90.83	89.1
0.1	0.761	0.716	2.042	92.39	92.83	89.79
0.15	0.679	0.566	2	93.25	94.33	90
0.2	0.698	0.573	1.938	93.01	94.23	90.31
0.25	0.686	0.581	1.903	93.13	94.18	90.48
0.3	0.674	0.875	1.730	93.19	94.11	91.34
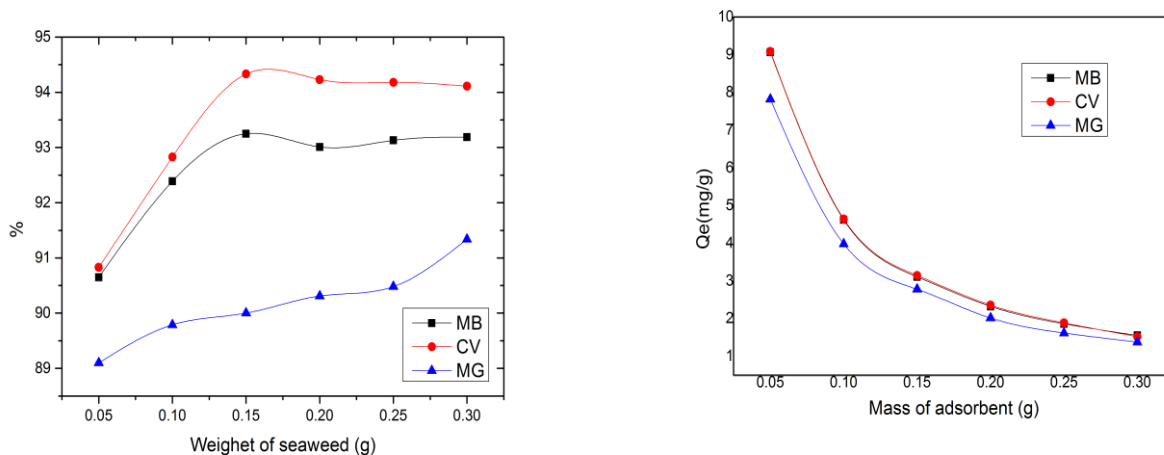
Figure(3.23) the effect of adsorbent dose on removal of (MB, CV and MG). At 10 ppm, pH3, 3h, and 25°C.

3.7.5-The ffect of particle size on removal of methylene blue, crystal violet and methyl green :

According to the results of the effect of particle size on the removal of MB, CV and MG dyes, note that the MB dye gave the highest percentage of removal. (97.27%, 91.59%, and 93.62%) respectively. In figure (3.24)the effect of particle size on (MB, CV and MG) removal can be remarked.

Table (3.14)the effect of particle size on dyes removal. At 10 ppm, pH 3, 3h, 25°C

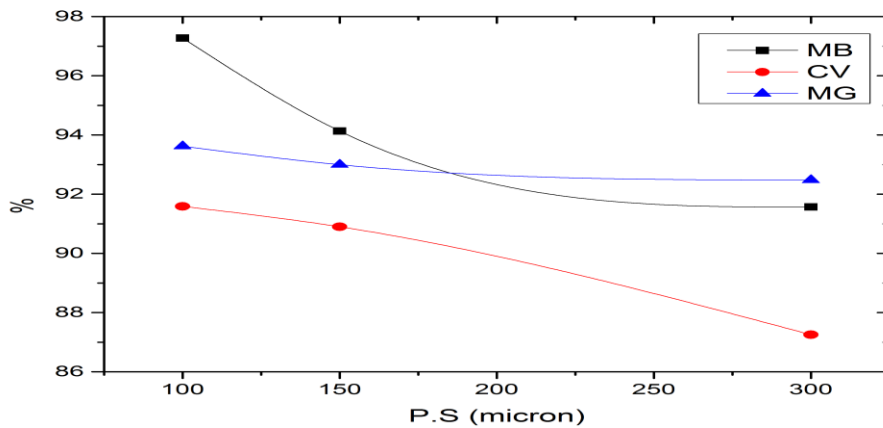| Particle Size (micron)	Average C_e (ppm)			Percentage removal (%)		
	MB	CV	MG	MB	CV	MG
100	0.272	1.681	2.550	97.27	91.59	93.62
150	0.587	1.819	2.794	94.13	90.9	93
300	0.843	2.549	3.004	91.57	87.25	92.48

Figure (3.24) the effect of particle size on removal of (MB, CV and MG). At 10 ppm, pH3, 3h, 0.15g of seaweed and 25°C.

3.7.6-The effect of Temperature on removal of methylene blue, crystal violet and methyl green :

From the results of the effect of temperature on the removal of CV, MB, and MG dyes, note that the CV dye gave the highest percentage of removal. (96.7%, 94.81%, and 91.98%) respectively. Figure (3.25)shows the effect of temperature on MB, CV and MG removal.

Table (3.15) the effect of temperature on MB removal. At 10 ppm, pH 3, 3h, 0.15g.

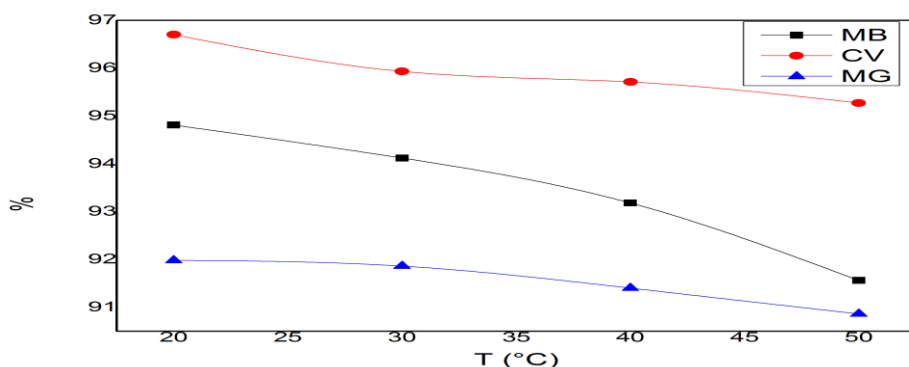| Temperature (°C)	Average C_e (ppm)			Percentage removal (%)		
	MB	CV	MG	MB	CV	MG
20	0.518	0.658	3.204	94.81	96.70	91.98
30	0.587	0.814	3.254	94.12	95.93	91.86
40	0.681	0.857	3.44	93.18	95.71	91.4
50	0.843	0.944	3.656	91.56	95.27	90.86

Figure (3.25) the effect of temperature on MB, CV and MG removal. At 10 ppm, pH 3, 3h, 0.15g of seaweed .

3.7.7-The effect of photolysis on removal of methylene blue, crystal violet and methyl green :

Results of the effect photolysis on the removal of MB, CV, and MG dyes, showed that the MB dye gave the highest percentage of removal. (95.38%, 92.65%, and 92.48%) respectively. In figure (3.26)more details can be seen on the effect of photolysis on MB, CV and MG removal.

Table (3.16) effect photolysis on dyes removal. At 10 ppm, pH 3, 0.15g, 25°C.

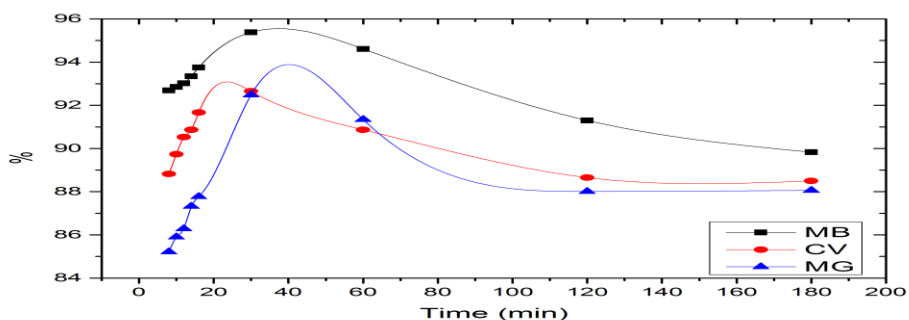| Time(min.)	Average C_e (ppm)			Percentage removal (%)		
	MB	CV	MG	MB	CV	MG
8	0.943	1.237	2.957	92.69	88.82	85.21
10	0956	1.025	2.819	92.85	89.74	85.9
12	0.951	0.946	2.742	93.02	90.53	86.28
14	0.912	0.912	2.534	93.34	90.87	87.32
16	0.896	0.833	2.445	93.75	91.67	87.77
30	0.679	0.734	1.503	95.38	92.65	92.48
60	0.873	0.912	1.731	94.61	90.87	91.34
120	0.969	1.134	2.398	91.3	88.65	88.01
180	1.151	1.235	2.957	89.83	88.82	85.21

Figure (3.26) the effect photolysis on MB, CV and MG removal. At 10 ppm, pH 3, 0.15g of seaweed and 25°C.

3.7.8-The effect of forigen ions on removal of methylene blue, crystal violet and methyl green:

From the results of the effect of foreign ions on the removal of MB, CV, and MG dyes, note that the MG dye gave the highest percentage of removal. (88.65%, 94.62% and 95.83%) respectively. Figure (3.27)shows the effect of salt or ions on MB, CV and MG removal.

Table (3.17) the effect of foreign ions on dyes removal. At 10 ppm, pH 3, 0.15g, 25°C

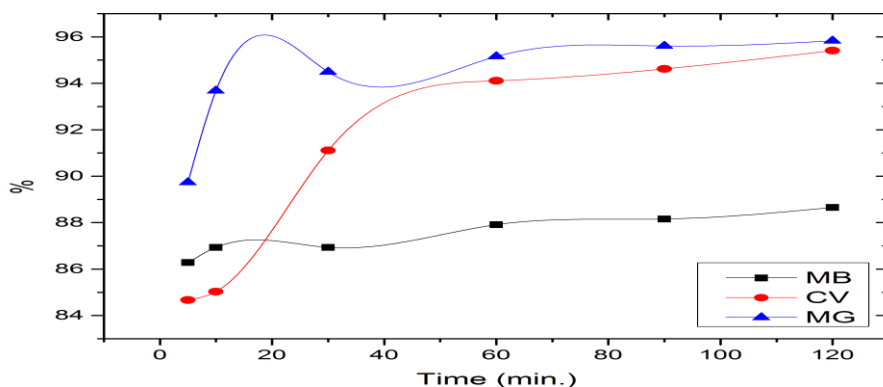| Time(min.)	Average C_e (ppm)			Percentage removal (%)		
	MB	CV	MG	MB	CV	MG
5	1.371	3.064	4.104	86.28	84.67	89.73
10	1.306	2.993	2.527	86.93	85.03	93.68
30	1.306	1.777	2.022	86.93	91.11	94.49
60	1.208	1.177	1.933	87.91	94.11	95.16
90	1.183	1.074	1.754	88.16	94.62	95.61
120	1.134	0.916	1.665	88.65	95.41	95.83

Figure (3.27) the effect of foreign Salt on removal of MB, CV and MG. At 10 ppm, pH 3, 0.15g of seaweed and 25°C.

3.8. Isotherm analysis:

The purpose of the adsorption isotherms is to relate the adsorbent concentration in the bulk solution and the adsorbed amount at the interface. The equilibrium isotherms in this study have been described in terms of Freundlich and Langmuir isotherms.

3.8.1. Langmuir Isotherm

The experimental result of Langmuir isotherm for uptake of MB, CV and MG on seaweed from Aqueous Solution is shown in table (3.18, 3.19, 3.20) of MB, CV and MG respectively. Langmuir constant calculated from graph is shown in table (3.21). Graphical representation of the same is shown in figure (3.28, 3.29, 3.30) of MB, CV and MG respectively.

Langmuir isotherm model also gives information about whether the adsorption process is favorable or not. For this purpose, dimensionless equilibrium constant which can be expressed below was used.

$$R_L = \frac{1}{1 + C_0 K_L} \qquad \qquad \text{... (1.3)}$$

The value of the isotherm to be either; Unfavorable ($R_L > 1$), Linear ($R_L = 1$), Favorable ($0 < R_L < 1$), Irreversible ($R_L = 0$) [20].

where K_L shows Langmuir isotherm constant (liters per milligram). All R_L values at different temperatures were calculated, and it was seen that all of them were between 0 and 1, showing favorable adsorption.

Table (3.18)the effect of concentration value on adsorption 0.15g seaweed, connect time 3h,pH 3 and at 25°C for MB.

C_0	C_e mg/l	Removal%	q_e	$1/q_e$	$1/C_e$
2.5	0.501	79.92	0.666	1.502	1.996
5	0.571	88.58	1.476	0.678	1.751
10	0.309	96.90	3.230	0.309	3.236
20	1.405	92.97	6.198	0.161	0.712
40	2.942	92.09	12.352	0.081	0.339
80	13.189	83.51	22.270	0.045	0.075

Equation	y = a + b*x	
Weight	No Weighting	
Residual Sum of	0.00517	
Pearson's r	0.99834	
Adj. R-Squar	0.99586	
	Value	Standard Err
1/qe Intercept	-0.0311	0.02044
Slope	3.76256	0.1084

Figure (3.28) Langmuir isotherm for MB onto 0.15g seaweed, pH 3, 3h, and at 25°C.

Table (3.19) the effect of concentration value on adsorption 0.15g seaweed, connect time 3h pH 3 and at 25°C for CV.

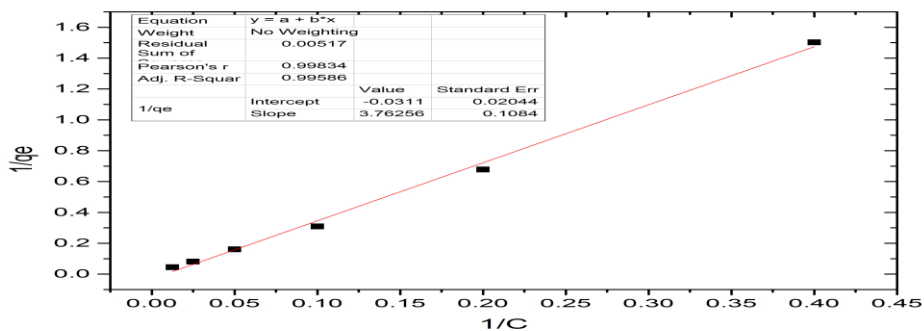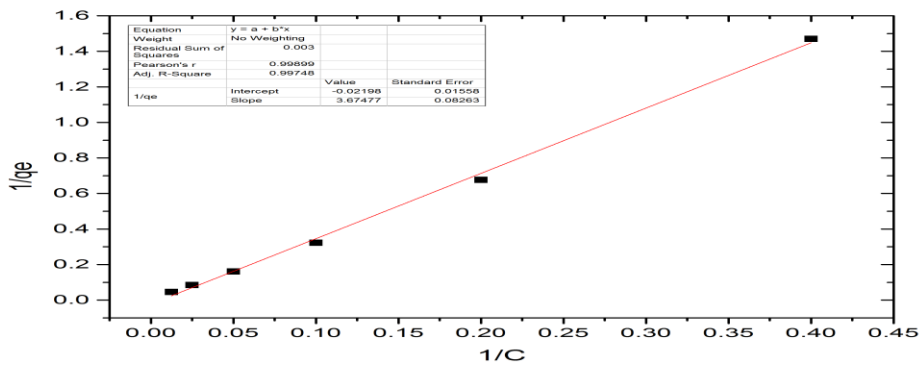| C_0	C_e mg/l	Removal%	q_e	$1/q_e$	$1/C_e$
2.5	0.458	81.64	0.680	1.470	2.183
5	0.568	88.62	1.477	0.677	1.761
10	0.739	92.60	3.087	0.323	1.353
20	1.278	93.60	6.240	0.161	0.782
40	4.9726	87.56	11.675	0.085	0.2011
80	14.864	81.41	21.712	0.046	0.067

Figure (3.29) Langmuir isotherm for CV onto 0.15g seaweed, pH 3, 3h, and at 25°C.

Table (3.20) the effect of concentration value on adsorption 0.15g seaweed, pH 3, connect time 3h and at 25°C for MG.

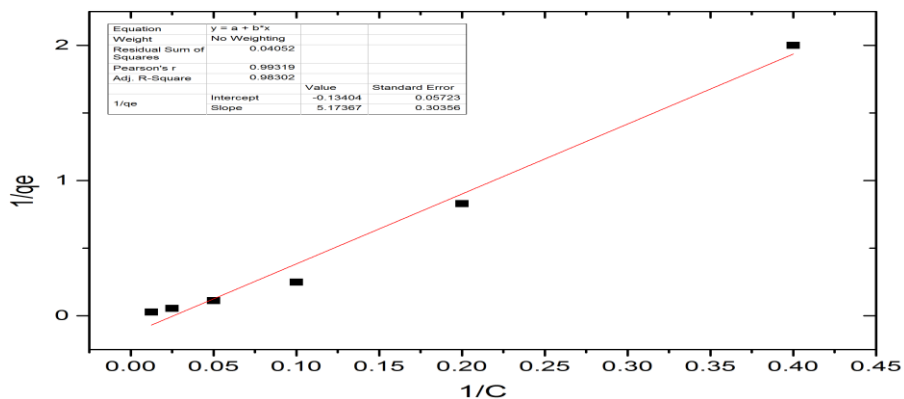| C_0	C_e mg/l	Removal%	q_e	$1/q_e$	$1/C_e$
2.5	1.5	40	0.5	2	0.667
5	2.59	48.14	1.205	0.829	0.386
10	1.937	80.62	4.031	0.248	0.516
20	2.021	89.89	8.989	0.112	0.495
40	3.171	92.07	18.415	0.054	0.315
80	7.975	90.03	36.012	0.027	0.125

Figure (3.30) Langmuir isotherm for MG onto 0.15g seaweed, pH 3, 3h, and at 25°C

The values of coefficient correlation R^2 for uptake of MB, CV and MG on seaweed obtained is in good agreement. The value of R^2 is (0.995, 0.997,

0.983) of MB, CV and MG respectivaly which is nearer to 1, indicates favorable adsorption. It indicates first layer of molecules adhere to the surface with energy comparable to the heat of adsorption for monolayer adsorption and subsequent layers have equal energies [46, 47]. Here we can say that Langmuir isotherm applies to each layer [47, 48]. The higher values of q_{max} (33.64, 45.35, 7.46) mg/g & K_L (0.991, 1.002, 1.000008) L/mg obtained for uptake of MB, CV and MG respectivaly on seaweed for Langmuir isotherm suggest better applicability of it. Thus uptake of MB, CV and MG on seaweed has a good fit for Langmuir isotherm.

3.8.2. Freundlich Isotherm

Results of modeling of the isotherms of MB, CV, MG adsorption by seaweed according to Freundlich isotherm model is summarized in table (3.13). Graphical presentation of the Freundlich isotherm is represented in figure (3.31, 3.32, 3.33) of MB, CV and MG respectivaly. Table (3.13) shows the Freundlich constants calculated from graph.

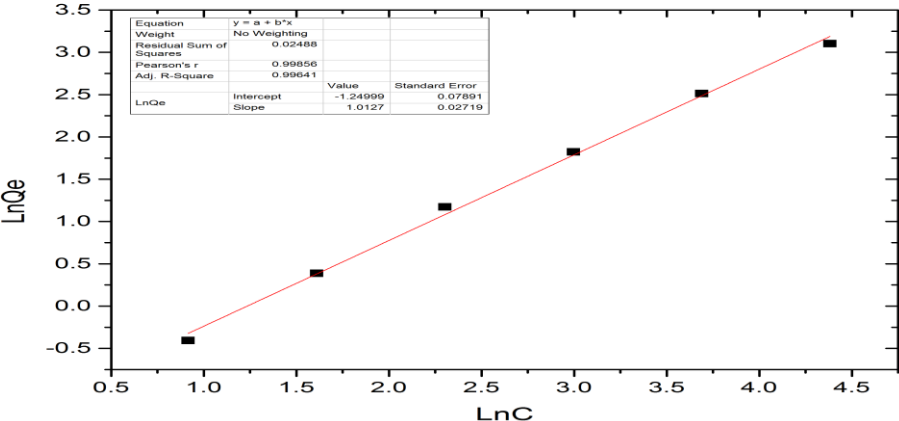| Equation	y = a + b*x	
Weight	No Weighting	
Residual Sum of Squares	0.02488	
Pearson's r	0.99856	
Adj. R-Square	0.99641	
	Value	Standard Error
LnQe Intercept	-1.24999	0.07891
Slope	1.0127	0.02719

Figure (3.31) freundlich isotherm for MB onto 0.15g seaweed, pH 3, 3h, and at 25°C.
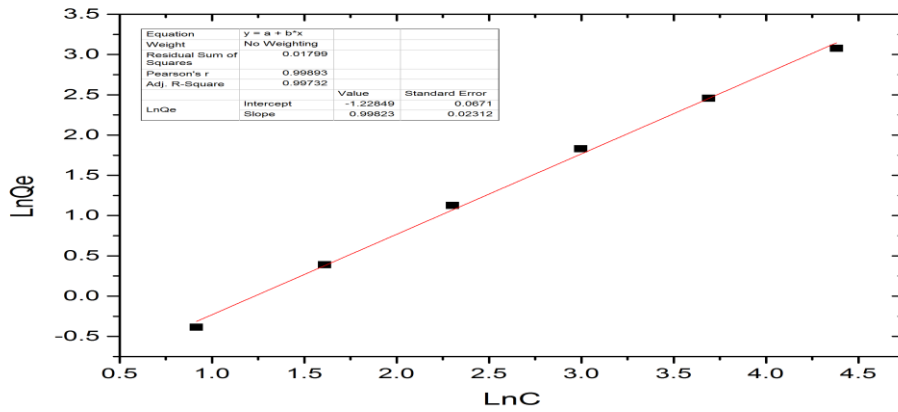
Figure (3.32) freundlich isotherm for CV onto 0.15g seaweed, pH 3, 3h and at 25°C
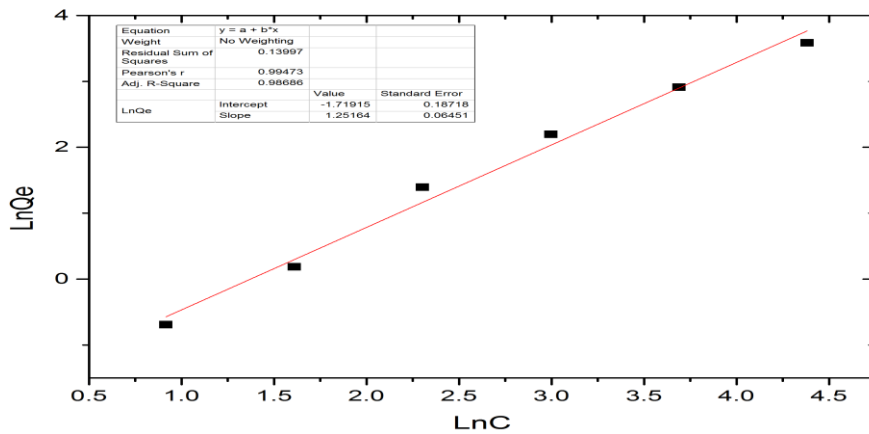
Figure (3.33) freundlich isotherm for MG onto 0.15g seaweed, pH 3, 3h, and at 25°C.

Here the value of K_F adsorption capacity (0.969, 0.978, 0.871) mg/g & adsorption intensity n (rate of adsorption) & (0.727, 0.272, 0.193) L/g of MB, CV, MG respectively is obtained from Freundlich isotherm. The value of n fulfills the condition (0 < n < 1) of Freundlich isotherm[46, 49, 50]. The values of coefficient correlation R^2 for uptake of MB, CV, MG on seaweed obtained is in a good agreement. The value of R^2 is (0.996, 0.997, 0.986) of MB, CV, MG respectively indicates a very good adsorption.

Table (3.21) the isothermal model adsorption data for MB, CV, and MG dyes.

Dyes	Langmuir				Freundlich		
	K_L	q_{max} (mg/g)	R^2	R_L	K_F	n	R^2
MB	0.991	33.64	0.99586	0.092	0.969	0.727	0.9964
CV	1.002	45.35	0.99748	0.0907	0.978	0.272	0.9973
MG	1.000008	7.46	0.98302	0.0909	0.871	0.193	0.9868

3.9- Determination of thermodynamic functions:

Table(3.23) presents the thermodynamic parameters at various temperatures. Enthalpy of adsorption (ΔH°), Gibb's free energy (ΔG°) and entropy of adsorption (ΔS°) for the determination of thermodynamics parameters are crucial as they contributes features on the final state of the system. Figure (3.34) show the van't Hoff plots in ln K_d versus 1/T. These parameters enable the justification whether the process is favorable under the thermodynamic point of view, the spontaneity of the system and if the adsorption process occurs with adsorption or release of energy. And we get the free Gibbs energy through the following equation(3.3):

$$\Delta G = - RT \ln \frac{Qe}{Ce} \qquad ....(3.3)$$

$$K_d = \frac{Qe}{Ce}$$

where K_d is equilibrium constant for adsorption, Q_e the amount of the dye adsorbed at equilibrium (milligrams per gram), C_e equilibrium concentration of dye (milligrams per liter), R is ideal gas constant (8.314 $Jmol^{-1}K^{-1}$), and temperature (kelvin).

Table(3.22)C_e, Qe and T values of the three dyes(CV, MG, MB) on seaweed.

T(K)	1/T	MB		CV		MG	
		C_e	Q_e(mg/g)	C_e	Q_e(mg/g)	C_e	Q_e(mg/g)
293	3.413×10^{-3}	0.518	3.161	0.658	3.114	3.204	2.265
303	3.3×10^{-3}	0.587	3.137	0.814	3.062	3.254	2.249
313	3.19×10^{-3}	0.681	3.106	0.857	3.047	3.44	2.187
323	3.09×10^{-3}	0.843	3.052	0.944	3.019	3.656	2.115
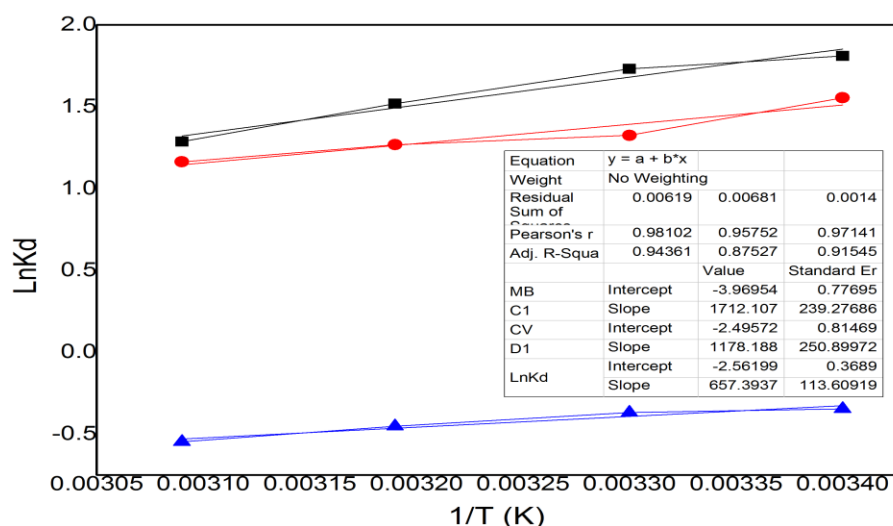
Figure (3.34) show the van't Hoff plots in In K_d versus 1/T

The negative values of ΔG° confirmed the spontaneity of methylene blue and crystal violet adsorption onto seaweed and the positive values of ΔG° confirmed the non-spontaneity of methyl green. It also suggests that the process is thermodynamically feasible. Negative ΔH° proves the exothermic nature for the adsorption process. The negative value of ΔS° was caused by the lack of randomness at solid/solution interface [51]. That is, in this case the

adsorption process may involve the formation of an adsorption layer with a thickness of several molecules of [52].

Table(3.23). Thermodynamic parameters for adsorption of MB, CV and MG dye onto Seaweed (T = 293, 303, 313 and 323 K)

Dyes	ΔG (KJ/mole) (T in K)				ΔH	ΔS
T(k)	293	303	313	323		
MB	-4.406	-4.36	-3.95	-3.456	-14.234	-10.778
CV	-3.785	-3.337	-3.299	-3.123	-9.795	-6.672
MG	0.845	0.929	1.176	1.468	-5.465	-6.933

3.10- Comparison this study results with previous studies:-

Table (3.24) Results of some scientific studies related to organic dyes removal

Sorbents	Textile dyes	pH	T (°C)	Langmuir $q°$ (mg/g)	Freundlich n
Seaweed. This study	Methylene blue Crystal Violet and Methyl Green	3	25	33.64 45.35 7.46	0.727 0.272 0.193
Posidonia oceanica[53]	Reactive red 228	5	30	5.74	1.65
Orange peel[54]	Procion orange	5.2	29	1.33	2.07
Apple pomace 5[55]	Reactive dyes	7.2	20	2.79	0.51
Activated sludge[56]	Reactive blue 2	2	25	0.96	1.16
Pichia carsonii[57]	Reactive blue 19	3	28	5	3.4
Kluyveromyces marxianus[58]	Cibacron orange	3	25	8.5	3.96
Rice husk[59]	Bismarck brown	3	27	84.4	1.95
Posidonia oceanica[60]	Methyl Violet	6	45	119.048	1.747
Orange and Banana peel[61]	textile effluent	7	30	0.0647 and 0.1808	0.108920 and 0.261643

Conclusions

Results presented in the current study clearly suggest the efficiency seaweed adsorbent for the removal of MB, CV, and MG dyes from aqueous solution. Batch adsorption experiments were carried out for the adsorption of the dye molecule from aqueous solution onto the seaweed at variation effect of different parameters . It was found that the maximum adsorption of the dye took place at an acidic solution pH. The effective solution pH, seaweed adsorbent dose, particle size, and temperature were found to be 3, 0.15g of MB and CV, 0.3g of MG, 100 micron and 20°C, respectively. At these experimental conditions, the dye removal efficiency of 96.9%, 92.6%, 80.62% for MB, CV and MG respectively was achieved. Three types of dyes have been tested using seaweed as adsorbent material and the best result was obtained using the CV dye. The removal process is affected by light, as the removal process decrease when highlighting the dye solution during the removal process with time. The rate of adsorption of the dyes for the seaweed reached equilibrium in 180 minutes for crystal violet, whereas 150 minutes for methylene blue and methyl green. Equilibrium and kinetic studies were conducted for the adsorption of the dye from aqueous solution onto seaweed adsorbent. The equilibrium data have been analyzed using Langmuir and Freundlich isotherms. The characteristic parameters for each isotherm and related correlation coefficients have been determined. The Langmuir and Freundlich isotherm was demonstrated to provide the best correlation for the adsorption of the dye. Experimental results indicate that the adsorption of methylene blue, crystal violet, and methyl green dye on the surface of seaweed decreases with increasing temperature, and this corresponds to the thermodynamic properties. It is noted from the negative enthalpy value that the exothermic process, and this is evidence that the process is an adsorption process only. This study shows that seaweed have a good potential to be

employed as adsorbent material in aqueous solution to resolve an environmental problem. The results obtained confirm that the low-cost material tested can remove dyes from aqueous solution. P. oceanica (Linnaeus) Delile is an endemic sea grass in the Mediterranean Sea where it is thought to play an important role in many cases such as supplying food and living place for other species, prevent-ing coastal erosion via equilibrating the sea floor, the life cycle of this sea grass are influenced by light, water, and sediment conditions and the urban as well as industrial waste, it is very important to note that P. oceanica is an endangered species because of various reasons based on pollution, the present study recommends only the use of dead leaves of P. oceanica for further and possible industrial studies[61]. Therefore, the present study offers the use of this accumulated biomass on the beach in an industrial mean instead of burning it.

Future work

1- Use of other types from seaweed.

2- Use of other types of dyes and compare the results.

3- Use laws and kinetic equations.

4- Use more devices evolution.

5- Take advantage of the ability of seaweed adsorption and use it to remove other types of paints, metals and other materials contaminated.

APPENDIX

Preparation of Adsorbent (seaweed):

WASH – DRY – CRUSH - SIEVE

100 micron   150 micron   300 micron of seaweed

Figure (2.2) Ground dead leaves of seaweed.

Practical steps for removing synthetic dyes from aqueous solutions by seaweed:-

Dyes   seaweed   pH   SWM 20

Dyes after adsorption   Centrifuge   spectrophotometer

Dyes after and before the adsorption process :

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