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An Efficient Removal of Bromophenol Blue Dye from Contaminated Water Using Nanographene Oxide as a Novel Adsorbent

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Committee Decision

We, the undersigned, approve the Master's Thesis of Sahar Zahran.

Thesis Title: An Efficient Removal of Bromophenol Blue Dye from Contaminated Water Using Nanographene Oxide as a Novel Adsorbent.

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Dedication

It was a long journey mixed with struggles and efforts with feelings of exhaustion of pleasure, pain to happiness and patience to surrender, and the fight to be what you dream of. I'm grateful to ALLAH ALMIGHTY for showers of blessings that were given to me having me reached my wanted destination and completing my research successfully.

My dedication includes a lot of people who walked with me through this journey. First and foremost, I would like to dedicate this thesis to my ***mother****, who was there always in my life to lighten up my pathways with her prayers. And to the soul of my* ***father*** *who taught me that to succeed you need to work hard. As well I would like to express my gratitude to my partner in life* ***Hatem*** *and my children,* ***Ahmad, Yara, Mariam,*** *and* ***Rafiq****. Without their tremendous understanding and encouragement in the past few years, it would be impossible for me to complete my study. Really, I loaded you much, love you all.*

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I'm grateful to my friend whose assistance was a milestone in this project with her frequent support ***Majdoleen Atawneh****, you are really a special person full of love, patience, and kindness. Many thanks to* ***Rasheeda Farhat*** *and* ***Razan Al Hroub*** *for their efforts with me. And finally, my dearest friend* ***Mai Abu Hassan*** *who believed in me through the way of my journey. Love you, my friends.*

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ARS	Acute radiation syndrome
BDCM	Bromodichloromethane
BPB	Bromophenol blue
BDD	Boron-doped diamond
C_e	Concentration at equilibrium
C_i	Initial concentration
CNT_s	Carbon nanotubes
CV	Crystal violet
DNA	Deoxyribonucleic acid
fGO	Functionalized graphene oxide
FT-IR	Fourier transform infrared
GO	Graphene Oxide
K_1	first-order rate constant (min^{-1})
K_2	Second-order rate constant (*g/mg.min*)
K_D	Distribution coefficient (*ml/g*)
K_f	Freundlich isotherm constant (*mg/g)*
K_l	Langmuir isotherm constant
MWCO	Molecular weight cutoffs
MWCNTs	Multiwalled carbon nanotubes
MB	Methylene blue
n	Freundlich constant related to the adsorption intensity
PPCPs	Pharmaceuticals and personal care products

PFO	Pseudo first order
PSO	Pseudo second order
q_e	Equilibrium adsorption amount (*mg/g*)
q_m	Maximum adsorption capacity (*mg/g*)
rGO	Reduced graphene oxide
R_L	Dimensionless separation factor
R^2	Correlation coefficient
rpm	Round per minute
SWCNTs	Single walled carbon nanotubes
SEM	Scanning electron microscope
THMs	tri-halomethanes
UV-vis	Ultraviolet-visible spectroscopy
VOCs	Volatile organic chemicals
%R	Percentage removal
ΔG°	Gibbs free energy (KJ/mol)
ΔH°	Enthalpy change (KJ/mol)
ΔS°	Entropy change (J/mol.K)

Abstract

A range of synthetic dyes released by industrial activities pose a threat to the protection of the environment. In this study the removal of bromophenol blue dyes (BPB), a form of synthetic dye, was successfully performed on graphene oxide nanosheets. The graphite oxide GO-450 nm was prepared by oxidation-reduction reaction (Hummers method). A tip sonicator was used to reduce the size particles to 200 nm under controlled conditions (time and power of sonication). The structure of these two sizes of GO was confirmed by scanning electron microscopy (SEM) and by statistical analysis. The oxygenated functional groups on the surface of both sizes of GO nanosheets were characterized by FTIR spectroscopy. The effect of several factors such as pH, adsorbent dose, contact time, initial dye concentration and temperature on the adsorption of BPB dye on GO particles was investigated. The adsorption isothermal data showed better fitting with Langmuir isotherm model than the Freundlich model. The adsorption capacities were found to be 28.57 mg/g and 40 mg/g for GO-450 nm and GO-200 nm after 40 minutes of contact time, respectively. The kinetic data for adsorption process obeyed a pseudo-second-order rate equation. The thermodynamic parameters such as ΔG, ΔH and ΔS were also determined, the obtained values indicated that the adsorption process was spontaneous and exothermic in nature.

Chapter One:

Introduction

1.1 Importance of Water

Water is a blessing of god. It's vital to life on our planet that dominates the surface of earth. Approximately 70% of the earth surface is roofed with water. All living things on earth must have water to survive, and it is considered as a biomolecule which means water is very important for all biological activities. Water makes up 55% to 78% of the human body, furthermore the principal part of the body cell [1].

Water shortage in many developing countries is being recognized as one of the foremost serious issues that affects the political and social fields at the present. Numerous diseases and harmful substances are transported and transmitted by water. Therefore, water quality is additionally a heavy factor to reduce the diseases occurrences.

Water stabilizes the temperature of earth and living things, acts as a transporter for everything like nutrients and waste, moreover it's the most content of blood and other aqueous fluids which acts as a transporter in human bodies and animals [2].

1.2 Types of Water Contamination

Contamination of water is a common concern worldwide. The reason for this issue is anthropogenic (man-made) or a geological contamination [1]. An anthropogenic contaminations are caused by human activities such as industrial activities, agricultural actions, commercial activities, residential and waste disposal systems, pharmaceuticals and personal care products [3]. The natural elements and compounds can contaminate groundwater when they are present at inappropriate amounts such as magnesium, calcium, chloride, nitrate, iron, fluoride, sulfates, or radionuclides. In addition to the decaying of organic particles, there are other natural elements and compounds that may contaminate water too by passing water through sedimentary rocks and soils

[4, 6]. Basically, the contaminants are four types : radiological contaminants, biological contaminants, inorganic contaminants and organic contaminants [1].

1.2.1 Radiological Contaminants

Many of the radiations originate from natural sources and man-made activities; therefore, the environment including water supplies is also contaminated by these radiations. The foremost sources of radiation to human come from the exposure to terrestrial and cosmic radiations, beside the breathing and ingestion of radioactive elements from water, food and air. Human exposure to radioactive elements is variable depending on the region, the quantity and also the composition of those radioactive elements different from area to another [6]. Thorium and uranium decay series, are naturally occurring radioactive elements; which will enter water and cause contamination. Strontium-90, carbon-14, iodine-131, and tritium (isotope of hydrogen) are samples of man-made radioactive elements which will be present in our drinking water. The concentrations of these elements are generally controlled so their levels in water are low [6, 7].

The effect of radioactive materials on the biological system is an acute effect or chronic effect reckoning on the term of exposure. High dose of radiations cause acute radiation syndrome (ARS), which has various effects on the organs that are responsible for blood forming, gastrointestinal and central nervous systems by killing the organ cells and destroying their tissues. While, a long-term or chronic exposure to radiation effects can cause cell damage or mutations to its genetic material (DNA), resulting in cancer or genetic abnormalities within the future generation [8].

1.2.2 Biological Contaminants

Bacteria, viruses, protozoa, algae and fungi are samples of biological contaminants that are found in water. These microorganisms are pathogenic and can cause diseases, especially in newborn, children, old people and people with a weak immune system. Typhoid fever, Cholera, Hepatitis-A are some of these water borne diseases that are a result of biological contaminated from food and water intake [1, 9].

1.2.3 Inorganic Contaminants

Natural sources and man-made operations play a good role in water contamination by inorganic substances. Major inorganic water contaminants are heavy metals, nitrate and phosphate group and other elements like chloride and fluoride [1]. The heavy metals are toxic to living things even at a low concentration. They are the foremost popular contaminants in water. Heavy metals like lead, mercury, cadmium, silver and others have several health effects on the body. Organs like the kidney, lungs, liver, blood, brain, nervous and genital system can be damaged and altered by heavy metals [4, 5].

Excessive level of nitrate and phosphate compounds mainly comes from the regular uses of fertilizers which might cause health disorders. Nitrates can transfer to nitrites within the system of humans. These nitrites oxidize the iron within the hemoglobin methemoglobinemia is created which may reduce the capacity of oxygen transported by the blood to other body cells [1]. This disorder is named methemoglobinemia and may cause other problems like anemia, cardiovascular disease, sepsis, metabolic troubles [10], muscle illnesses and heart strokes [11].

High level of phosphate can cause kidney failure and osteoporosis. Moreover, the phosphorus in appropriate amounts plays a main role in bone and teeth formation beside its function in the body of protein synthesis. An excessive amount of phosphate in water bodies can speed up eutrophication (a reduction in dissolved oxygen in water bodies). As an example, phosphate feeds algae in water results algal bloom that produce high toxin and reduce the entrance of sun light which can cause the death of living bodies in water [12].

Chlorine is the major water disinfectant used. The legal concentration value that’s used as a water disinfectant is nontoxic to humans [13]. Harmful effect of long-term use of water chlorine is shown in respiratory system disorders and diseases such as asthma and cardiovascular diseases, also chlorine can cause cancer by combining with natural compound and produce chlorination byproducts, these byproducts are highly carcinogenic and may stimulate the free radicals within the body, leading to cell damage [14]. Fluorides are employed in various pharmaceutical products, tooth pastes, disinfectants. Undesirable effects of fluoride can cause skeletal and dental fluorosis, Alzheimer disease and some kind of dementia [1].

1.2.4 Organic Contaminants

Almost all organic compounds either present or man-made exists in every place of environment; they may be within the main sources of water contaminations. Industrial developments play a vital role in raising the number of artificial organic compounds, as a result a rise within the health problems risks by the presence of these compounds in water [15]. The most organic contaminants will be discussed below. Therefore, the dye is discussed as a significant contaminates during this thesis.

1.2.4.1 Trihalomethanes (THMs)

Some naturally organic occurring compounds found in water by the decay of vegetation [16], my react with chlorine within a disinfection process and produce trihalomethanes compounds [17].

Trichloromethane (chloroform), bromodichloromethane (BDCM), are examples of trihalomethanes compounds, that are referred to as disinfection by-products [18]. An outsized amount of these (THMs) are released into the air. Chloroform that is found in treated water is different from any other kind of (THMs), because it may be released to water during the chlorination process and enters into our bodies by skin (showering, swimming, washing), inhalation or by drinking water. High doses of chloroform cause various health problems that affects the liver, kidney, heart and nervous system. Besides that, chloroform can increase the incidence of cancer [19].

1.2.4.2 Volatile Organic Chemicals (VOCS)

Volatile organic chemicals (VOCS) are a branch of carbon-containing compounds, due to its high volatility as it can easily spread into air, so diffuse to water. Many of the commercial and industrial products may be accountable for volatile organic compounds water contamination. These include solvent (benzene, toluene), cleaning agents (tetrachloroethylene), paints, inks, dyes and pesticides products, and from gasoline and oil spill [20]. Kidney and liver defects, neurological and reproductive problems, birth abnormalities and cancer are a number of the health cases that are caused by VOCS water contamination [1].

1.2.4.3 Pesticide

Pesticides are used to protect the plants against weeds, fungi, insects and other pests, quite immeasurable loads of pesticides are consumed around worldwide. Depending on the used quantity of pesticides, acute and chronic health effects is caused especially within the developing countries because they are still using the cheaper pesticides which are more toxic and less selective. The consequence of pesticides on human health depends upon the type of pesticides ingredients.

Neurological, blood and genetic disorders, birth defects, endocrine disruption and benign or malignant tumors production probability increase [1, 21].

1.2.4.4 Raw Materials of Plastic Manufacturing

Preservative, coloring, plasticizers and other additives that are basic substances of plastic manufacturing that may also contaminate water within a producing procedure or directly by using plastic equipment [20]. A number of these compounds are considered to be chemicals disrupt the endocrine functions (endocrine-disrupting chemicals), the plasticizer like phthalates and bisphenol-A (raw materials that are used for plastic production) are samples of these compounds [22].

1.2.4.5 Pharmaceuticals and Personal Care Products (PPCPs).

Pharmaceutical and personal care products (PPCPs) are a category of chemicals that used for human health care as prescription or over- the- counter medicines, cosmetics and veterinary applications boost the expansion of livestock [23]. These products and their metabolite contain chemical ingredients that goes into water by excretion of the living things, discharge of unused and expired products and chemical waste of producing [24]. Pharmaceuticals like antibiotics, anti-inflammatory, analgesic, hormones, chemotherapy agents and personal care products may cause disruption of the gland and cause cancer [1].

Pharmaceuticals and personal care products (PPCPs) are considered to be an ‘Emerging organic contaminants’, these contaminants continuously are present in the environment and cause potential effects on public health with very low and chronic exposure [1] . Pesticides, illicit drugs, life style chemicals (nicotine, caffeine), hormones, industrial additives, by-product, surfactants, flame/ fire retardants and contaminated water treatment by products are also samples of emerging organic compounds [25] .

1.2.5 Dyes

Despite the fact that they add color and a new outlook to almost everything in the world, are the most organic contaminants. Consumption and contamination of water are results of several anthropogenic activities that use dyes either of natural or synthetic origins. Quite 100,000 various dyes and pigments are employed in the industry. The estimation of (17 to 20%) of business pollution comes from textile dyeing and finishing processing, additionally to its toxic effects, the dyes are xenobiotic compound that the priority of the dye contamination has been boosted [26, 27].

Currently the uses of dyes became necessary as a large range of their uses within the industrial applications, like food, pharmaceutical, cosmetics, paints, leather, paper, textiles, rubber, plastic and printing inks productions, agriculture research, photography and in many other domains that can be compatible with modern lifestyle [27]. The continual loading of dyes effluents which contain organic and inorganic compounds to water will promote dangerous issues to water bodies and every living thing on the earth. The extensive use of dyes in many industries, release synthetic dyes into the environment has become a significant issue worldwide within the recent years. The textile and fabric dyeing industry is that the main sector that are playing a task within the consuming and also the pollution of water [28], large percent of nearly 70% of produced dyes are utilized in textile industries. Furthermore, great amount of water is employed within the textile and fabric treating leading to high level of liquid effluents, around 200 L of water is consumed for 1 kg of textile production [29].

The production of dyes is near to 800,000 tons every year. At the time of dyes manufacturing not all dyes can adhere to the fabric leading to large percent of these dyes are being discharged to the water depending on the type of dyes. Around 50% of the reactive dyes and 2% of the basic dyes may be drained to water as water effluent pollutants [26].

Even natural dyes that are easily biodegradable compared to synthetics dyes have a specific restriction in its uses because of their influences on the environment. They are obtained from plants, insects, fungal and microbial origins. To stabilize and fix the natural dyes onto fabrics, substances called mordents are required, they are metal salts like chromium salts. Many health problems and toxic effects may be occurred by draining these metals salts to water during textile dying procedures. Furthermore, large amounts of water are consumed through dying of materials by using natural dyes [30]. Natural dyes are mostly utilized in food industry, while synthetic dyes in general are used for fiber textile [26].

The dangerous impacts of dyes on the environment and living things are increasing due to the release of intense by-products that are occurring in wastewater produced by special chemical processes as hydrolysis, oxidation, or other mechanisms on dyes [1]. Furthermore, the existence of naphthol, Sulphur, nitrates, heavy metals like lead, chromium, arsenic, nickel, cobalt, mercury and other chemicals such as soaps, enzymes that have chromium compounds that act as an auxiliary agent to extend the standard of textiles dying processes produce high toxic effluents of dyes. Some are cancerous and serious by-products, resulted from the reaction of hazardous chemicals likely being in water such as softeners, dye fixing agents of formaldehyde, removers of chlorine and non-biodegradable dyeing compounds with water disinfectants especially chlorine [31].

1.2.5.1 Properties of Dyes

Dyes are colored compounds that have a special structure nature, they absorb light in spectrum at certain wavelength (400-700 nm), table 1 shows the wavelength of light absorption versus color in organic dyes [32]. They need a minimum of one chromophore group which is chargeable for dye color; also, they have a conjugated system and stability within the forces of compound thanks to electrons resonance. Usually, chromophores are a component that contains one or more functional group of delocalized electron system with conjugated double or simple bond (with a more or less extended p electron). Hetero-atoms like nitrogen, sulfur and oxygen with non-bonding electrons are involved in the structure of chromophore. Chromophores generally have - N=N- (azo), C=S (Sulphur), =C=O (carbonyl), =C=C=, C=NH, -CH=N-, NO or N-OH (nitroso) [26]. In addition to chromophores, dyes also contain other groups which are auxochromes. Their name belongs to their action that enhances the color, they are polar groups as carboxylic acid, sulfonic acid, amino, and hydroxyl groups, they’ll bind to the textile polar group. Furthermore, they are used to influence dye solubility [32].

Table 1. Wavelength of light absorption versus color in organic dyes [33].

Wave Length Absorbed (nm)	Color Absorbed	Color Observed
400-435	Violet	Yellow-Green
435-480	Blue	Yellow
480-490	Green-Blue	Orange
490-500	Blue-Green	Red
500-560	Green	Purple
560-580	Yellow-Green	Violet
580-595	Yellow	Blue
595-605	Orange	Green-Blue
605-700	Red	Blue-Green

Dyes are often classified according to their sources, or fiber type, the application methods and as the chemical structure.

1.2.6 Classification of Dyes

1.2.6.1 Classification of Dyes According to their Sources

Dyes are obtained either from Naturally or synthetically sources. Dyes were naturally derived such as herbs, plants, trees, lichens, and insects. As time passed natural dyes gradually began to fade, and synthetic dyes began to take their place for many reasons. Synthetic dyes are economical, readily available, and simple to use [30].

1.2.6.2 Classification of Dyes According to the Fiber Type

Dyes may be named supported the category of fiber that may be used as dyes for nylon, silk, wool or polyester [34].

1.2.6.3 Classification of Dyes According to the Application Methods

Another classification of dyes depends on the methods of application and their affinity to the substrate (fabric types). Application methods are often categorized to direct, reactive, disperse, vat, acidic and basic dyes. The common dyes applications and toxicity be included in table 2.

Table 2. *Classification of dyes depends on the methods of application* [35].

Dyes	Applications	Toxicity
Reactive	Wool, cotton and flax	Allergic conjunctivitis, rhinitis, occupational asthma, skin irritation
Direct	Leather, paper and cotton	Bladder cancer
Disperse	Nylon, polyester, acrylic fiber and cellulosic fibers	Carcinogenic and skin allergy
Vat	Fiber of cellulose [36]	
Acidic	Wool, leather, nylon, silk, paper and ink-jet printing	carcinogenic
Basic	Nylon, paper and as septic agent in medicine	carcinogenic

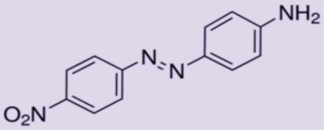
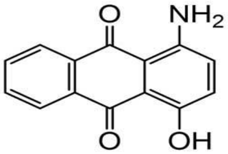
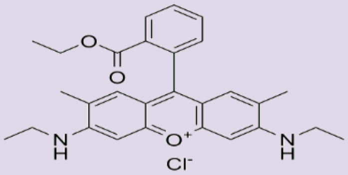
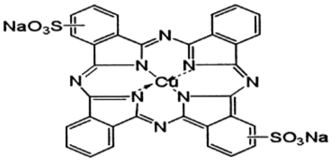
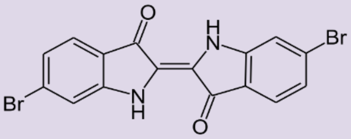
1.2.6.4 Classification of Dyes According to the Chemical Structure

The classification of dyes that is preferred is based on their chemical structures. Most classes of dyes that have a good range of uses within the industry are azo, anthraquinone, xanthene, phthalocyanine and indigoid dyes [26]. Samples of the most chemical structure classes are shown in table3 below. Azo dyes are the foremost important class, accounting for over 60% of all industrial dyes. It's considered the primary dye in various industrial applications as in cosmetics, pharmaceutical, leather, paper, food and fabrics manufacturing. The function group that represent this class is (N=N) group, which attaches to two groups that a minimum of one in each of them is aromatic, but usually both are aromatic [37]. Classification of azo dyes is in step with the quantity of azo groups within the backbone of one dye. Mono, diazo, triazo, polyazo contains single, double, triple or more of an azo groups [26]. As a result, wide range selection of colors are obtained from the range of azo dyes structures [37]. According to the dye importance the anthraquinone is that the second class. These classes of dye are shaped by anthraquinone body but its structure is colorless. To grant their color, donor groups are introduced to the structure [34]. Anthraquinones dyes are characteristically known with their bright colors and an ideal stability which is a bonus to use them giving us an improved quality upon application [38].

Xanthene dyes also are considered a vital class due to their application in many fields. They are used for dyeing fibers like silk, cotton and wool, more over as for paper, wood, leather, foods and cosmetics dyeing [39]. Also, they are used as laser dyes, as fluorescent dyes and as organic dyes for several medical diagnoses. Furthermore, they are applied in biology and pharmaceutical field due to their characteristics like antibacterial, antiviral, anti-inflammatory, anticancer, antioxidants and insecticides [40]. Their structure is predicated on two benzene rings fused by pyran ring when introducing auxochrome group usually OH to the structure. They are radiant in color and have wide selection of color shades [39]. Phthalocyanines are a type of synthetic aromatic macrocyclic organic compounds. They are made up of four iso-indole unity linked by nitrogen atoms. Therefore, the extended delocalization of the π-electron system in their structures makes them to soak up light deeply, in the subject of IR region. Many of metal ions can create coordination complexes with phthalocyanines [38]. Copper phthalocyanine (direct blue 86) is the best coordination form that offers the right color and properties of the dyes. Phthalocyanines have extensive uses in paint and printing inks [34]. Indigo dyes are natural blue compounds that are obtained from plant to dye fabric in blue especially denim jeans.

Nowadays indigo dyes are chemically synthesized, synthetic indigo compounds are better in quality than natural form, also, they have very important application fields like medicine and cosmetics [38].

Table 3. Classification of dyes depends on the chemical structure [34].

Chemical group of dye	Example
Azo Dyes **Ex. Disperse Orange 3**	
Anthraquinone Dyes **Ex. Disperse Red 15**	
Xanthene Dyes **Ex. Rhodamine (basic red 1)**	
Phthalocyanine Dyes **Ex. Direct Blue 86**	
Indigo Dyes **Ex. Tyrian Purple**	

Both dye and fiber structures are playing a job on the dyeing process. Subsequently, determinate the mechanism routes of bonding between them. Natural and man-made fibers will be employed in the industry. The common naturals are cotton, silk, leather, silk, fur, linen, flax and hemp jute. Besides natural fibers, polyester, polyamide (nylon), polypropylene which are examples of man-made fibers [41]. Covalent, ionic, hydrogen and Van der Waals forces are the classes of bonding which will be occurred between dye particle and fiber. When chemical action run between dye and fiber the bond is made. Heating resistant and powerful bond are going to be occurred with fixed color that can’t be easily become pale when exposed to the sunlight and chemicals. A bond takes place when two opposite charged sites of every dye and fiber are attracted. Mainly strong salt linkage is going to be occurred between the acidic dyes that containing carboxylic or sulfonic group and also the basic group within the wool matrix, the result’s good fastness of acidic dyes wash. Hydrogen bonding is resulted between dye and fiber when there’s a robust electrical attraction between them, likely polar fibers undergo this sort of bonding. The last class of chemical bonding is Van der Waal forces, it’s the weakest bond that be formed between molecules [42].

1.2.7 Influences of Dyes on Environment and Health

The enormous production and also the wide scale use of the appliance of synthetic dyes are answerable for many environmental and health impacts [28]. The molecular entities of most dyes usually are complex and inert which provides them the steadiness and difficulty to biodegrade [27]. Not all dyes have affinity on the fabrics once they are applied during dyeing process of textile; some amount of dyes are discharged to water reckoning on the kind of materials that are dyed. The result’s high concentration of dyes found in the effluent of textile dyeing [43]; moreover, the organic dyes have high solubility in water [28]. Unwanted changes and effects on the environment and health are resulted from the direct effluents of these colored substances into water [44].

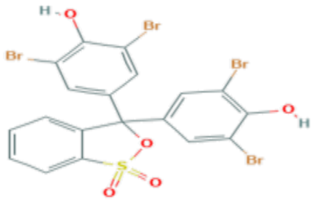
Mutagenicity, carcinogenicity, immune system depression, kids hyperactivity (ADHD) and toxicity can be caused by long run exposure of dyes. Acute or accidental exposure can cause respiratory sensitization by affection on the immune system after inhalation [27, 43]. Mainly the harmful effects of dyes in mammals and aquatic living things come from products that are created from the biodegradation of dyes. The foremost common dyes that are released to the environment are the azo dyes; they undergo to an anaerobic reduction process in reciprocally aromatic amines are produced, which are considered to be very dangerous compounds. Most of them are mutagenic and carcinogenic which are linked to splenic sarcomas so as bladder and liver cancer [26].

Another issue in concern of the textile industry is over 8000 of chemical compounds are consumed within the dyeing and printing procedure of textiles; most of them have impacts on the health either directly or indirectly. Ethanoic acid, oil of vitriol, ammonium sulphate, hydrated oxide, peroxide and other are samples of these chemical compounds [31].

1.2.8 Bromophenol Blue Dye

Bromophenol Blue dye (BPB) is the dye that was used as a contaminate during this study. Another name is tetra-bromophenol blue, the main points of BPB dye are shown in table 4 below [45].

Table 4. *Bromophenol blue dye properties* [46].

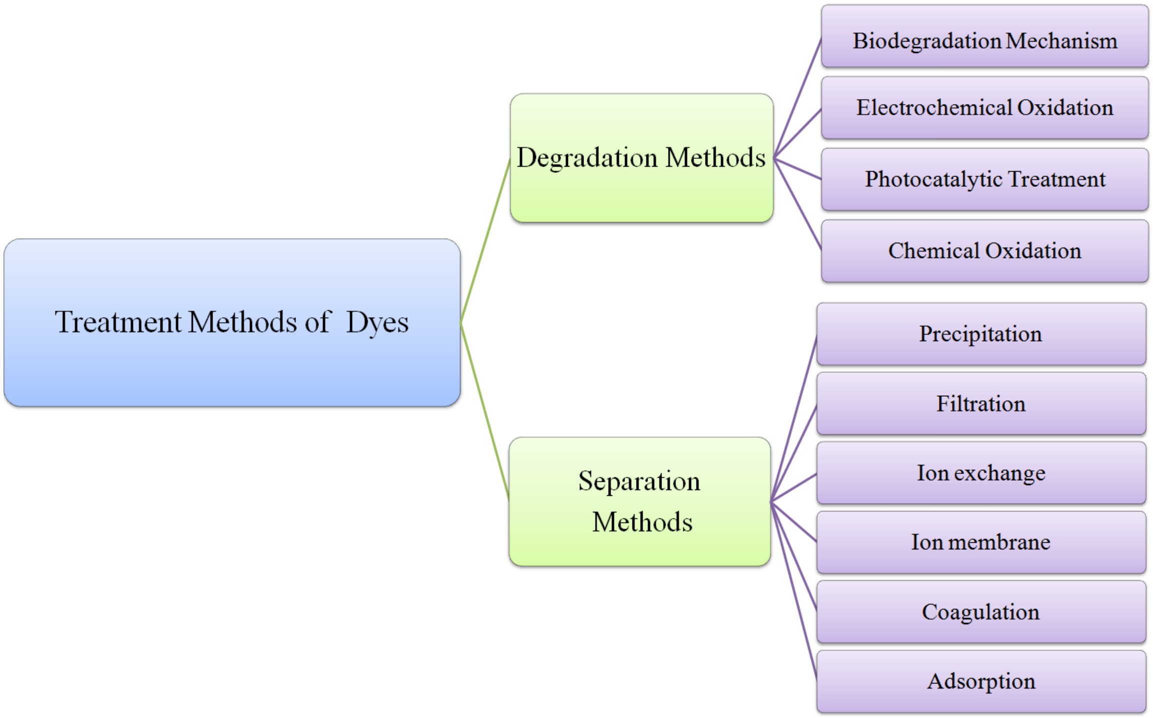
Structure	
Chemical Formula	$C_{19}H_{10}Br_4O_5S$
Synonyms	Tetra-bromophenol blue Bromophenol blue sultone form Tetra bromophenol sulfonphthalein
Molecular Weight	670 g/mol
Class	Triaryl - methane

Bromophenol blue is a member of triaryl-methane dyes group. Triphenylmethane dyes conjure around 30-40% of total dyes consumption [47]. BPB acts a pH indicator, as at neutral pH absorbs the red light most strongly and transmits blue light; therefore, the solutions of the dye are blue. At low pH, the dye absorbs the ultraviolet and blue light strongly and appears yellow within the solution. In a solution at pH 3.6 (in the center of the transition range of this pH indicator) obtained by dissolution in water with none pH adjustment, the characteristic green, red color of tetrabromo-phenolsulfonephthalein is where the apparent color varies counting on the concentration and/or path length from which the solution is detected [45] .

BPB dye is used in many industrial applications like cosmetics, textiles, foods and inks of printing, it's convenient for laboratory uses as an acid-base indicator, stain for biological media (proteins, nucleic acids) and as a tracking dye gel electrophoresis [44]. Triphenylmethane dyes are aromatic xenobiotic compounds. It's supposed that they are carcinogenic and mutagenic to humans and which mammalian cells exhibit high toxicity [47]. Moreover, the health effects are caused by bromophenol blue dye depends on exposure route, it should cause respiratory and digestive tract irritation also dermal and eyes irritation. Injury of the cornea or conjunctiva of eyes may be caused by exposure to dyestuff dye [46, 48].

1.3 Treatment Methods of Dyes

Methods are used to treat the water from dyes can be classified into biological, chemical, and physical. additionally, various combinations of treatment techniques have been used to boost the efficacy of water treatments. Degradation and seperation mechanism are utilized in water treatment from dyes, they are another classification that's supported the mecahnism way within the treatment processes [49]. The scheme 1 shows the foremost conventional methods are used.



Scheme 1. *Treatment methods of dyes.*

1.3.1 Degradation Methods

Biodegradation mechanism of dyes is completed by using the microorganism like fungi, algae and bacteria (in aerobic and anaerobic conditions), additionally to enzymes from different biological sources.

The biological methods or bioremediation is cheap economic, and it considered as a green clean mechanism. Generally, it acts on the bond of chromophore groups within the dye by breaking them [50]. Chemical oxidation otherwise of dyes degradation like ozonation, electrochemical oxidation, photolysis techniques [49]. The efficiency of an ozonation technique depends on the affinity of the dyes chemical structure to the ozone [51]. One more method for the treatments of water which is revealed as a sophisticated chemical oxidation. Potent oxidizing agents like oxide radicles are produced which have excellent degradation ability for dyes. The high consumption of energy and therefore the consumption of chemical regents are the restrictions of this method [26].

Also, dyes are oxidized to simple inorganic compounds like water and carbon mono-oxide by electrochemical oxidation. It's an efficient process with reasonable amount of energy to supply the applied current for electrode activation. Different types of electrodes are used like metal, mixed metal, graphite and carbon electrodes. High cost of effective dye degradation anodes like boron-doped diamond (BDD) is taken into account as a limitation for using this method [52].

Photolysis or photocatalytic treatments are another technique of dye degradation method. By using UV light, the photochemical reactions are administrated and therefore the bonds of the dye compounds are broken and converted to simpler compounds. The presence of catalyst as peroxide will accelerate the dyes degradation [49].

1.3.2 Separation Methods

Dyes are organic compounds with a structure that can't undergo biodegradation. Thus, separation methods which include physical and physio-chemical methods are convenient tactic for dye removal from water. Precipitation, coagulation, ion exchange, membrane filtration and adsorption are an example of the separation treatment of dye effluents [27].

Precipitation method will be one amongst the preferable options to get rid of them. $CaCO_3$ compound is employed as precipitant of dyes. It's simple and functional methods for the organic compounds removal. On another hand, massive sludge is formed with continuous large supply of chemicals is required [29]. Chemical coagulation technique involves the addition of several coagulants either natural as cactus or chemical as alum, lime, iron salt and polymer ferric produce huge complexes with the dye by the reaction of their positive charge with the negative charge of dye units that are precipitated as sludge. Generally, this system is followed by filtration to promote the sludge separation [51]. Coagulation method is used as a main or a secondary treatments process. The benefits of this process are cheap, low within the consuming of energy and also the availability of various forms of coagulants in markets. However, the constraints of this methods are the formation of giant sludge amount of harmful chemical residue that are contributed of some adverse health and ecology impacts [52]. Electro-coagulation is one more technique that the coagulation of negatively charged dyes is caused by the appliance of an instantaneous current between metals electrodes immersed within the effluent, which cause the dissolution of electrode plates into the effluent. The metal ions can form coagulant species and metal hydroxides that aggregate or precipitate the contaminants. Aluminum or iron anodes are used, it's a low in cost technique with no chemical additives are needed [53].

Ion exchange, during this method anions in the effluent are exchanged for one more anion from an exchanger. The resin (exchanger) acts as a medium to facilitate ion the reactions, it's an organic polymer either be natural or synthetic that form a network of hydrocarbons, over the polymer matrix are action sites, that are called functional groups with positive or negative charge is made on the polymer network. These functional groups readily attract ions of an opposing charge. It's considered to be simple operation with no loss of adsorbent by regeneration. However, it is not efficient operation for all dye types [50].

Membrane filtration is a vital branch of separation methods that don't demand a chemical reagent; they need a capability to separate, concentrate and clarify dyes from effluents supported membranes that might be permeable or semi-permeable with different pore sizes, which has the flexibility to trap some effluent molecules by delimiting their motion. The main classes of membrane filtrations are reverse osmosis, nanofiltration and ultrafiltration. These classes are categorized reckoning on their ability of retained the solute particles in the step with their relative molecular weight cutoffs (MWCO). Thus, it’s a very important to pick out the suitable pore size of membranes depending on the kind of dye or the contents of wastewater. Reverse osmosis can retain the solute particles which are about 1000 MWCO, nanofiltration that acts on the particles within the range of 500-15000 MWCO, while the ultrafiltration between 1000-100 000 MWCO, it is an option to remove large particles like resin and polymer [26]. Reverse osmosis has superb dye removal efficiency, but it is deemed as high in cost technology. Whereas, the dye removal efficiency of nanofiltration membrane lies between ultrafiltration and reverse osmosis, therefore, it’s a preferable thanks to trap the dye from water with lower cost than reverse osmosis [54]. Considered a costly operation with endless renewal of the equipment because of the membrane plug [51].

Adsorption is one amongst of the foremost functional process for the treatment and removal the soluble and insoluble organic or inorganic of the contaminants. It’s the most feasible treatment process, because it’s economically favorable, easy handling and high selection of various adsorbent materials are available. These adsorbents can be natural like zeolites, clay minerals, charcoal and ores, or synthetic that may be obtained from polymeric materials, various cultivation products or wastes and wastes of many fields like industrial, domestics and sewage. Nowadays, nano adsorbents have a special interest to deal with them due to their superior adsorption character in the removal of various types of toxic organic and inorganic substances. Recently, because of the advantageous of adsorption method, the researchers concern to search out adsorbent with low cost and high removal capability of pollutants [52]. Phenomenon and mechanism of Adsorption, also several adsorbents that are applied for water treatments of dye effluents, are debated within the next chapter.

As it was mentioned before, the dyes are considered to be one amongst the foremost organic contaminants that are found within the effluents. Furthermore, most of the dyes are toxic, non-biodegradable and stable in numerous conditions, as a result there's a limitation to use one single method for treatments. While, conjunction of several methods for effluent treatment is convenient and may take off over 85% of the contaminant [31]. The common merits and demerits of effluent treatment methods are summarized in the table 5.

Table 5. *The merits and demerits of effluent treatment methods* [50].

Method	Merits	Demerits
Biodegradation	-Green technique -low cost	-Biological and degradation -By-product formation -Slow process -Special conditions and large work are needed
Chemical oxidation (ozonation)	-Easy method -No sludge formation	-Production of carcinogenic organic compounds -Limited effect
Advanced chemical oxidation	-Effective method	-High cost -High energy and chemical energy demand
Electrochemical oxidation	-Effective method -Low energy demand	-High cost and anodes
Photolysis	-None hazards -Simple compound formation -No sludge formation	-Electricity cost
Precipitation	-Simple operation -Effective method	-Massive sludge formation -Continuous supply of chemicals
Electrocoagulation	-Simple method -No chemical additives -Low in cost	-Sludge formation
Ion exchange	-Simple operation -Regeneration of adsorbent	-Not effective for all kind of dye
Membrane filtration	-No chemical reagent is needed	-Sludge formation -High cost -Contentious renewal of equipment
Adsorption	-Simple and effective method -Flexible operation design -Inexpensive process	-Non-selective process -Regeneration -Waste product

1.3.3 Types of Adsorbents

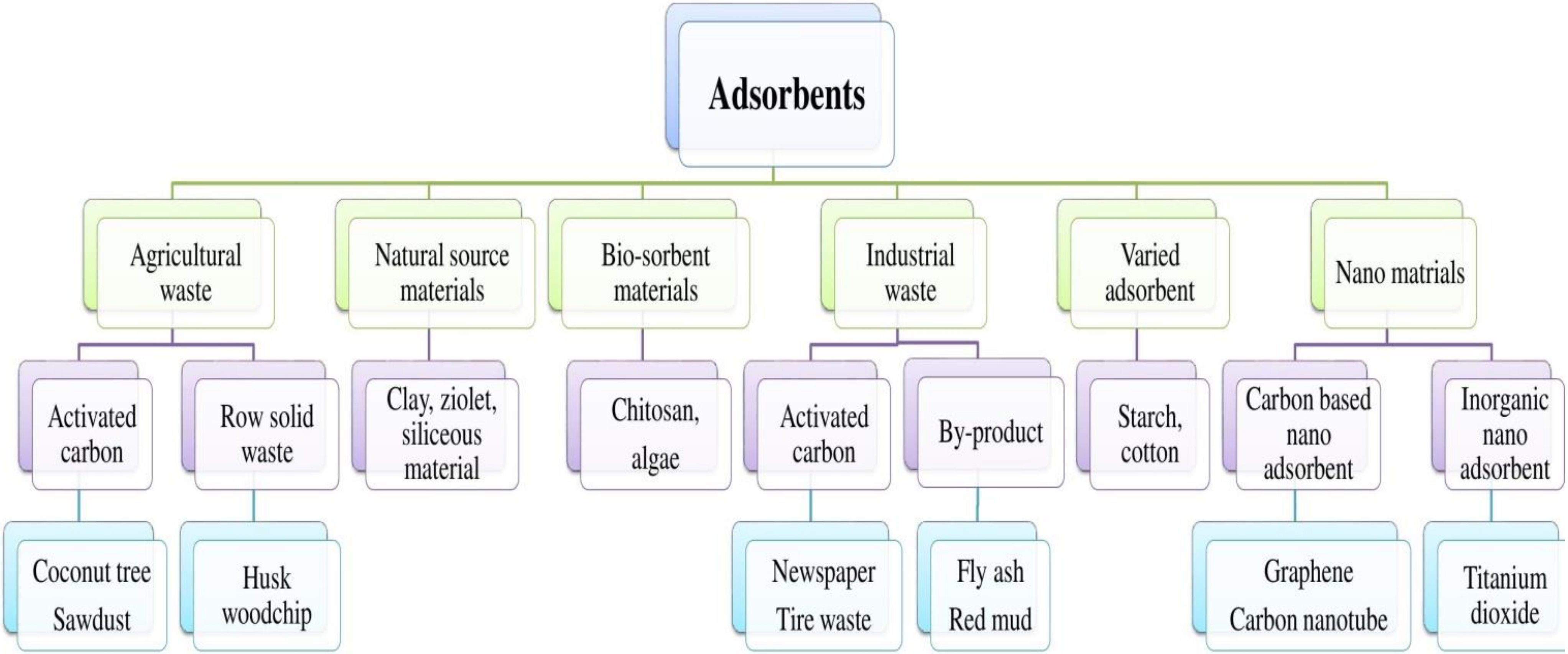
It’s evident that the features of adsorption and also the structure of adsorbents have a key role to play with their use in many applications. Features that would have an effect on the removal of contamination are an adsorption capability, unique expanse, pore size, grain size and pore size distribution, They are so critical to any change so the elimination will shift, too [55]. Among other wastewater treatment technologies, adsorption has to alleviating the dye concentration within the effluents. So as that a broad kind of solid materials, different in chemical types and geometric surface structures, are used as adsorbents for the removal of dyes. Scheme 2 presents one among the classifications of various sort of adsorbents that are utilized in the treatment of dye-containing wastewater [56].

Adsorbent of agricultural waste may be categorized into two groups: 1) Activated carbons 2) solid waste of agricultural waste in crude form and also the waste that are resulted from agricultural industries. Agricultural waste is one of the foremost popular products to be used as activated carbon. Agricultural waste adsorbents are inexpensive and that can minimize waste out of it by reusing. Other sources of adsorbents are the by-product and activated carbon solid materials from the commercial waste. Fly ash and red mud are a standard sort of non-conventional adsorbent of industrial waste by-products. Moreover, the adsorbents from natural sources conventional like zeolite, activated alumina and silica gel, and non-conventional materials like clay and siliceous materials. Biosorbent based of both living and dead organisms’ adsorbent. Chitosan and algae or fungal biomass are included within the biosorption process. The last class of adsorbents are non-conventional materials as starch and cotton, they are sorted under miscellaneous class [51, 57].

Among these materials activated charcoal which is the adsorbent of choice and produces the best results as it can be used to remove different dyes. Carbon is additionally identified as solid sponge [57, 58]. In general, commercial activated carbons are the foremost powerful adsorbents because of their excellent ability to adsorb organic contaminates, and if the adsorption process is correctly built, they need affordable quality performance. The flexibility of its adsorption is especially thanks to their structural characteristics and micro-porous texture, which supplies them a large surface area. Also, their chemical composition, which can be modified to vary their properties by chemical treatment so greater level of surface reactive sites [59].

Lately, diversity of low expenses and environmentally agreeable nano-scale materials are introduced to permit rapid and effective removal of the dyes with ascending rate of industrial contaminants discharge into water like titanium dioxide nanoparticles, graphene and carbon nanotubes [60, 61].

A number of carbonaceous nanomaterials and their applications in water treatment will be mentioned within next subsections.



Scheme 2. *The classifications of different adsorbent used in the treatment of dye-containing wastewater*

1.3.4 Carbonaceous Nanomaterials

Carbonaceous means any organic material with high carbon content. The "carbon” is the essential element of life. It represents the sixth element in the periodic table [62]. Carbon is the third most abundant element on the earth. Carbon may occur in an exceeding number of various forms. The foremost common allotropes of carbon are graphite and diamond. Graphite consists of stacked carbon sheets of hexagonal structure with sp^2 hybridization. carbon forms a tetrahedral lattice diamond with sp^3 hybridization, a metastable form of carbon [59].

Nano technology has been used to develop sort of carbonaceous materials whose dimensions aren’t greater than nanoscale with new properties and capacities that qualify them to be used as an energetic adsorbent. Carbonaceous nano-adsorbents have an oversized reactive surface, effective adsorption rates with the minimum dose of materials and may be synthesized at a lower cost compared to activated charcoal [63]. With regard to the removal of dyes, variety of nano adsorbents are categorized in keeping with their types and dimensions (D). Nanoparticles (0D), (1D) as nanofibers and nanotubes, nanosheets (2D) and nanoflowers (3D). In terms of dimensionality, the various classes of dye nano-adsorbents are shown in figure 1 [64].

Graphene-based nano adsorbents, carbon nanotubes (CNTs), fullerenes are examples of carbonaceous nanomaterials in several dimensions that are used as adsorbents for water treatment. As described above, nanostructured adsorbents provide a wide extent with an optimum adsorption power. This adsorption potential either physically or chemically is improved by surface functionalization, and therefore the porosity available is promoted [56].

Beside to the environmental treatment, the carbonaceous nanomaterials have widespread interest in several applications relying on their outstanding of thermal and electrical conductivity, also the mechanical strength (high flexibility and high tensile strength) properties, including medical domain as drug delivery, catalysis, super capacitors, air filtration etc. [63].

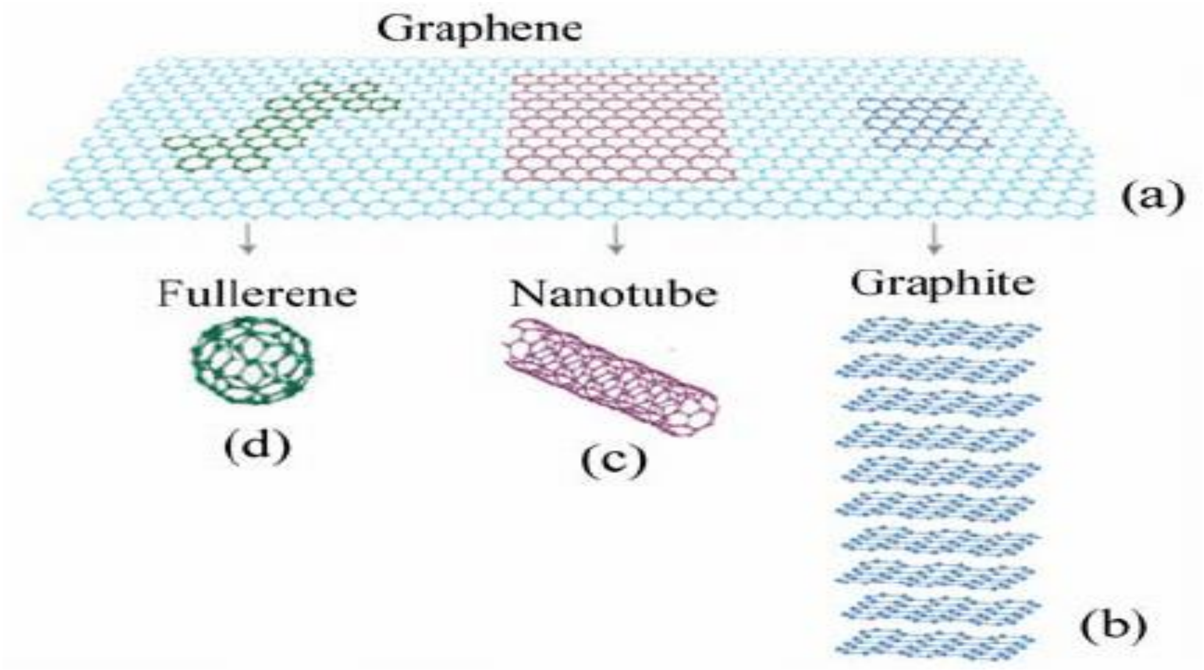


Figure 1. Different dimensions of carbon-based nano adsorbent.

1.3.4.1 Graphene (G) and Graphene Oxide (GO)

Graphene is a two-dimensional (2D) carbon allotrope. It's composed of one layer of sp^2 hybridized in a hexagonal structure that may look like a chicken wire mesh. Graphene is additionally treated as a basic building block of another carbon structures. It's wrapped in fullerenes (0D), rolls in carbon nanotubes (1D), and stacked in graphite (3D). By exfoliation of natural graphite can graphene nano sheets be obtained [60, 65].

Many sheets layered on top of each other are considered to be multi-layer graphene, to the point where the material becomes graphite. 3D crystal graphite could be relatively popular material – utilized in pencil tips, battery forms and far more.

Graphene has a wonderful mechanical stability; it seems to be one in all toughest materials ever tested. Measurements have shown that graphene incorporates breaking power 200 times above steel. Furthermore, is one in each of the thinnest identified material. These properties open brand-new vision in the industrial sector like cars and plane production by replacing metals with carbon-based materials as graphene paper. Also, graphene incorporates a higher thermal, electrical conductivity and a higher mobility. Therefore, graphene performs of heat ten times better than copper and conduct electricity higher than copper even at room temperature [62].

Graphene may be a potent adsorbent for treating contaminated water, it's potential extent nearly of 2630 m^2/g considerably greater than many materials. Even so, the challenge of controlled graphene synthesis with a limited number of layers and tiny yields, etc. stays to be treated. As a derivative, graphene is mostly used, e.g., graphene oxide (GO), reduced graphene oxide (rGO), or functionalized graphene oxide (fGO). All derivatives of graphene are prepared by GO modification. The foremost popular method of GO synthesis is graphite oxidation, followed by exfoliation [62]. The structure of rGO is between graphene and GO, there are just some functional groups on the surface of the rGO [63].

Graphene oxide (GO) is a potentially high 2D adsorbent for removal of dye that's derived by chemical oxidation of graphene. Through different methods specifically Hummer's method, the graphene is subjected to heavy oxidation by strong oxidants as $KMnO_4$ or $NaNO_2$ beside to a robust acid like sulfuric or nitric acid. As a result, nanosheets are formed are fully of oxygenated functional groups like alcohols, epoxides and carboxylic acids thus they react with functional water contaminants. GO is therefore hydrophilic and simply be exfoliated in water [65, 66].

1.3.4.2 Carbon nanotubes (CNTs)

In the world of nano adsorbents, the invention of carbon nanotubes opened a replacement term. Carbon nanotubes also called buckytubes consist a tubular layer of graphene or graphite rolled up during a nanometer diameter and a length of a spread of micrometer with hemispherical ends as fullerene structure. They have a 1D shape with a diameter in nanoscales and a length of micrometer. CNTs show unique characteristics associated with their shapes, they are hydrophobic materials, have huge specific area, rich hollows with layered structure, of high number of pores size and π-conjugative structures, leading to a large range of remarkable applications in wastewater treatment, including the elimination of organic pollutants and heavy metals [63].

The two general types of CNTs are single-walled carbon nanotubes (SWCNTs) with a one layer of graphene rolled up into a cylinder and multi-walled carbon nanotubes (MWCNTs) with a variety of graphene cylinders rolled along with an interspace; they are presented in figure 2. The absence of functional groups is challenging in their adsorption performance. They are loaded by different materials to boost the adsorption capacity like chitosan, thiol group, Fe3O4 magnetic nanoparticles, polymers, etc. Therefore, the assembly of functionalized CNTs capable of adsorbing a good range of cationic and anionic dyes is great importance [64].

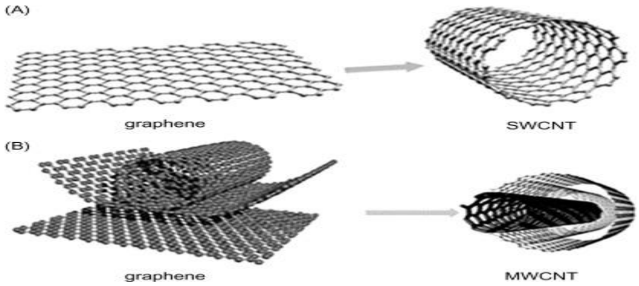


Figure 2. *The two general types of CNTs.*

1.3.4.3 Fullerene

Buck minster fullerene was the primary fullerene to be discovered, it’s a carbon allotrope including cluster of 60 atoms of carbon combined to create spherical molecules [62]. This molecule was named after the American architect Buck Minster Fuller because its structure resembles the framework of the dome-shaped halls designed by Fuller for an outsized industrial exhibition. Fullerenes are hydrophobic in nature, but on fictionalization, they might even be converted into hydrophilic and amphiphilic, also, to spice up its ability for various applications [60, 61].

1.4 Adsorption Phenomenon

Adsorption is a surface phenomenon whereby a substance (adsorbate) is accumulated on the surface of a solid (adsorbent). The adsorbate can be either in a gas or liquid phase, as shown in figure 3. As we mentioned in previous sections, the adsorption phenomenon is the foremost commonly method used to evaluate the adsorbate capability to bind with adsorbents [59].

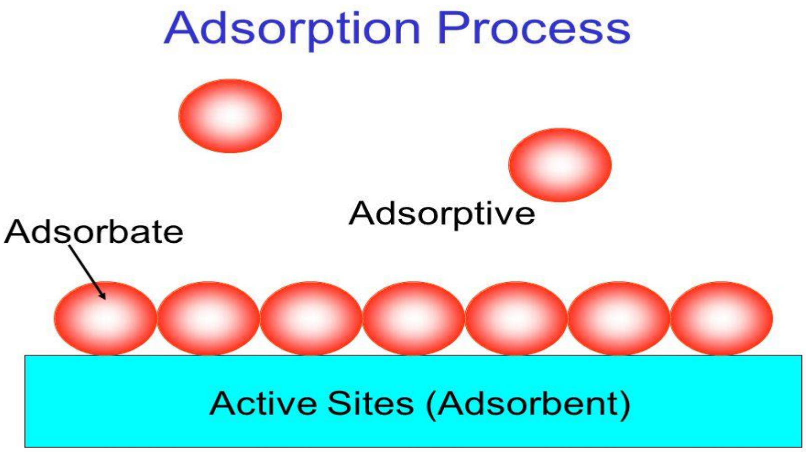


Figure 3. *Modeling of adsorption process* [67].

Generally, there are three components: the adsorbent, the adsorbate and the waste water which plays a role in the strength of adsorption in waste water treatment by adsorption technique. They are presented in figure 4 as ternary system. Usually the key force guiding adsorption is the affinity between the adsorbent and the adsorbate [59]. Moreover, comparing with the affinity of adsorbate for the adsorbent, the power of a molecule to adsorb could be a result of its affinity for water. The more hydrophobic contaminant it has the greater power to depart from aqueous solution and to be adsorbed on the surface of an adsorbent [68].

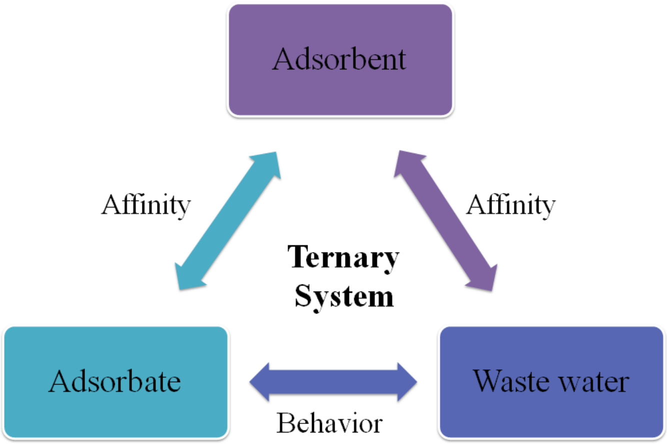


Figure 4. The relationships between the three components of an adsorption system.

The adsorption exists either a physical adsorption or a chemical adsorption supported the interactions between the adsorbent and adsorbate [62].

1.4.1 Physical adsorption

Physical adsorption or physisorption, originates when the interparticle bonds are weak bonds as van der walls, hydrogen and electrostatic forces between the adsorbate and adsorbent through the formation of single or multiple layers of adsorbent on the adsorbent surface. Physical adsorption is reversible type [62, 69].

1.4.2 Chemical adsorption

It is classified as chemisorption, and presented by creation of an adsorbate layer bound with strong interparticle bonds due to the electron exchange as covalent or an ionic bond to the adsorbent surface, it is an irreversible process [62, 69].

1.5 Study of the Adsorption Mechanism of BPB Dye into GO

The adsorption mechanism is usually categorized as physisorption or chemisorption, that the nature of bonding relies on the function groups of species that are involved within the adsorption process. Furthermore the modification on the surface of adsorbent by introducing functional groups are often administrated to extend the bonding formation between adsorbent and adsorbate, thereby, arise within the removal of adsorbate [62].

The GO nano-adsorbents have oxygen functional groups like carboxylic acids, epoxides, alcohols. Thus, it can react with the anionic organic dye as BPB dye by physical binding. There are many factors that effects the adsorption mechanism mostly the pH factor. It regulates the ionization and dissociation of functional groups that are related for both the BPB dye and GO [70].

There are many kinds of interactions between GO adsorbent and BPB adsorbate consistent with their structure nature. The π-π interaction that occurs between the majority π systems on GO and the aromatic ring retained within the structure of BPB dye. The second bonding is bond forming between the carboxyl or hydroxyl group of GO and the hydroxyl group of BPB dye. Also, the electrostatic attraction may be attributed between an anionic dye and therefore the positive charge of GO at low pH [47].

1.6 Adsorption Equilibrium Studies

Adsorption performance and features of the adsorbents are studied for various adsorption isotherms, kinetic and thermodynamic models to elucidate the effect of various parameter on the adsorption process and therefore to establishing the right model of adsorption [71].

The percentage removal and the concentration of dye retained within the adsorbent phase (the equilibrium adsorption amount) q_e(mg/g) are determined by equation 1 and 2, respectively:

$$\%R = \frac{C_i - C_e}{C_i} \times 100\% \quad (1)$$

$$q_e = \frac{(C_i - C_e)}{m} \times V_L \quad (2)$$

Where C_i (mg/L) is the initial concentration of dye as adsorbate,C_e (mg/L) is the concentration at equilibrium for adsorbate dye, V (L) is the volume of sample, m (g) is the mass of adsorbent [44].

1.6.1 Adsorption Isotherm Model

Isotherm model is employed to judge the magnitude relation between the adsorbate and the adsorbent. It's also an equation touching on the number of solute adsorbed to the solid q_e and also the concentration of solute within the solution C_e at a fixed temperature and a particular solution pH [69].

They are many isothermal models usually fitted for the relation between q_e and C_e, but the foremost common models utilized to quantify the dye adsorbed on the adsorbent are Langmuir and Freundlich adsorption isotherms [26]. The coefficient of correlation (R^2) of the two models is obtained and decides which model is the best model for batch adsorption [71].

1.6.1.1 Langmuir Isotherm

The Langmuir model assumes that the adsorption of adsorbate molecules occurs on a homogeneous surface by monolayer adsorption with no interaction between adsorbed molecules. The model assumes uniform surface adsorption energies and no adsorbate transmigration within the plane of the surface. Supported these assumptions, the subsequent equation 3 describes the linear Langmuir model [72] :

$$\frac{C_e}{q_e} = \frac{1}{K_L \times q_m} + \frac{C_e}{q_m} \tag{3}$$

Where,$\mathrm{C_e}$ is that the concentration of dye at equilibrium (mg/L),$\mathrm{q_e}$ is that the adsorption capacity at equilibrium (mg/g), $\mathrm{q_m}$ is the maximum adsorption capacity (mg/g) and $\mathrm{K_L}$ (L/mg) is Langmuir isotherm constant. A plot between $(\mathrm{C_e}/\mathrm{q_e})$ vs. $(\mathrm{C_e})$ graph gives of $1/\mathrm{K_L} \times \mathrm{q_m}$ and $1/\mathrm{q_m}$ as the intercept and slope, respectively [44].

From Langmuir constant can calculate the dimensionless separation factor $\mathrm{R_L}$, it determines the adsorption nature, either the adsorption process is favorable or not. The equation 4 represents a way to calculate $\mathrm{R_L}$ factor, the $\mathrm{R_L}$ values are described in table 6 [73].

$$R_L = \frac{1}{1 + K_L C_i} \tag{4}$$

Table 6. *Sort of adsorption isotherm supported the $R_L$value.*

Value of $\mathrm{R_L}$	**Adsorption**
$\boldsymbol{R_L > 1}$	Unfavorable
$\boldsymbol{R_L = 1}$	linear
$\boldsymbol{0 < R_L < 1}$	Favorable
$\boldsymbol{R_L < 1}$	Irreversible

1.6.1.2 Freundlich Isotherm

Freundlich model is helpful because it effectively explains isothermal adsorption data for several organic pollutants [68]. The fundamental assumption is that the formation of multilayers by adsorbate molecules on the adsorbent surface, thanks to the various affinities for various active sites on the adsorbent surface [44]. The linear Freundlich isotherm is shown in equation 5:

$$ln\, q_e = ln\, K_f + \frac{1}{n} ln\, C_e \tag{5}$$

Where, q_e is the adsorption capacity at equilibrium (mg/g), C_e is the concentration of BPB dye at equilibrium (mg/L), K_f (mg/g) is the constant associated with the adsorption capacity of the adsorbent for the adsorbate, and n is the constant associated with the adsorption intensity and therefore the adsorbent heterogeneity. The constants (n) and (K_f) of Freundlich isotherm are calculated by linear plot (ln q_e) versus (ln C_e) from the slope and intercept, respectively [72]. If 1/n value is equal one it means the adsorbent is homogeneous with a regular pore size and surface chemistry; but, if 1/n values are less than one which shows much of heterogeneity that are resulted from diversity within the shapes and sizes of the adsorbent pores as activated carbons. Table 7 shows the kind of adsorption isotherm according the value of 1/n [73].

Table 7. *Type of adsorption isotherm supported the 1/n value.*

$\frac{1}{n}$ **value**	**Type of isotherm**
$\frac{1}{n} = 0$	Irreversible
$0 < \frac{1}{n} < 1$	Favorable
$\frac{1}{n} > 1$	Unfavorable

1.6.2 Kinetic Isotherm Model

The utmost parameter to think about while designing an adsorption system is adsorption kinetics. It describes the retention or release of a solute from an aqueous environment to solid-phase interface at a given adsorbents dose, temperature, flow rate and pH. Pseudo-first-order and pseudo-second-order are commonly used models to predict the adsorption kinetics of the foremost organic compounds. They can be used to induce the solute adsorption process into an adsorbent, as well as studies the rate of adsorption to reach of equilibrium through the process, and also provide data on how other variables, such as pH, time, etc., that affect the action in order to build a fast and effective model [62, 71].

The kinetics models analyze the experimental data to manage the mechanisms of the adsorption process, like diffusion control and mass transfer. The suitability of any model depends on the error level-correlation coefficient (R^2) [71].

1.6.2.1 Lagergern's Pseudo-First Order (PFO)

The relationship between the speed of occupancy of the adsorbent sites and therefore the number of vacant sites is explained by the pseudo-first-order kinetic model [58]. It's stated in the differential form as given in the equation 6 [74].

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \tag{6}$$

The PFO model linearized form is presented in equation 7 [44]:

$$ln\ (q_e - q_t\ ) = ln\ q_e - K_1 t \tag{7}$$

Equation7 is commonly used to fit the kinetics data and calculate the parameter K_1 and q_e for different initial concentrations of adsorbates were calculated from the slope and intercept respectively by plotting as x-axis versus $\ln(q_e - q_t)$ as the y-axis. Where: q_t is the adsorption capacity at any time t (mg/g), q_e is the adsorption capacity at equilibrium (mg/g) that is estimated by the PFO model, k_1 is the first-order rate constant adsorption min^{-1} and (t) time (min) [75].

1.6.2.2 Ho's Pseudo Second Order (PSO)

PSO model suggests that the adsorption of solute rate is proportional to the available sites on the adsorbent. It's the most model utilized in the research papers for predicting the adsorption experimental data and calculating the constant adsorption, it's given by the following equation [74]:

$$\frac{dq_t}{dt} = K_2 (q_e - q_t)^2 \tag{8}$$

The rearrangement of equation 10 gives the following equation in order to compute the parameters of the model:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \tag{9}$$

Where: q_e is the adsorption capacity at equilibrium (mg/g), q_t is the adsorption capacity at any time t (mg/g), (t) time (min), k_2 is the rate constant for the pseudo-second order adsorption (g/mg.min). The plot of (t) at the x-axis and t/q_t at the y-axis of the equation gives a linear relationship from which (k_2) and (q_e) are determined from the intercept and slope of the plot, respectively [75].

1.6.3 Thermodynamics of Adsorption

Thermodynamic parameters like standard enthalpy change (ΔH°) and standard entropy change (ΔS°) are calculated using the equation 10 of Van't Hoff, and the values for standard free energy (ΔG°) are determined from the equation 11:

$$ln\frac{q_e}{C_e} = -\frac{\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R} \tag{10}$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \tag{11}$$

In equation 10: (ΔH°) is the standard enthalpy change (KJ/mol), (ΔS°) is standard entropy (J/mol.K), q_e is the adsorption capacity at equilibrium (mg/g), C_e is the concentration of BPB dye at equilibrium (mg/L), (R) is the ideal gas constant (8.314 J.mol/K), (T) is the temperature (K). In line with equation 10 the values of (ΔH°) and (ΔS°) are calculated from the slope and intercept of a plot of ($\ln q_e/C_e$) versus (1/T), respectively. Where in equation 11 (ΔG°) is the standard Gibbs free energy (KJ/mol) [76].

Thermodynamic parameters ΔG°, ΔH° and ΔS° are indicators of the possible nature of adsorption. The negative or positive value of (ΔH°) is an indicator that either the adsorption reaction is exothermic or endothermic respectively. Also, a negative value of (ΔS°) represents a decrease in the entropy, in contrast the increasing in the entropy is presented by positive value. The degree of spontaneity of an adsorption process is indicated by (ΔG°), a negative value represents energetically desirable adsorption, while the positive value of (ΔG°) indicates non-spontaneous adsorption [71].

1.6.4 Factors Affecting Adsorption Capacity

Different factors, such as adsorbent dosage, contact time, pH, initial dye concentration and temperature may affect the adsorption. Optimization of those variables often extended to the full-scale treatment process for the removal of dyes through facilitating the adsorption process [56].

1.6.4.1 The Adsorbent Dosage and its Properties

The dosage of the adsorbent is an important parameter for determining the capacity of the adsorbent for a given quantity of adsorbate under operating conditions. In general, an increasing of the adsorbent dose provides more area so more binding site of adsorbent are available [56].

Other conditions to be properly considered when choosing an adsorbent supported the following subsequent criteria: low cost and readily available, acceptable mechanical properties, high physical strength (not disintegrating) in the solution, long life and has regenerative ability if necessary, etc. [59]. The regeneration of adsorbent is completed by eliminating the adsorbate molecules through shifting the distribution of equilibrium via several methods. Regeneration may be achieved when treating an air or wastewater drain with contacting the adsorbent with a clean gas or liquid. Another method to regenerate the adsorbent by contacting it with solvents that have affinity for the adsorbate, like using ethanol or other polar solvent to regenerate a hydrophobic polymer. Additionally, a process called temperature swing adsorption, raises the temperature. The exothermic existence of the adsorption mechanism is useful by this approach. Options involve regeneration using steam or hot gas in situ [57].

1.6.4.2 The Concentration of Adsorbate.

A defined mass of adsorbent can only adsorb a set amount of dye, which is why the initial concentration of dye within the effluent is one among the important factors to be studied. The effect of the increase within the initial dye concentration would increase the loading capacity of the adsorbent by decreasing the available adsorption sites. This result in decrease within the performance removal of dye or other contaminants. Therefore, the share of dye removal relies on the initial concentration [56, 70].

1.6.4.3 The Effect of Contact Time

The contact time between adsorbent and adsorbate has a major impact on the adsorption capacity. Commonly, the speed of dye removal increases to a specific degree with arise in time to an extent, further increase the time wouldn’t increase the uptake, because of the buildup of the dye on the present adsorption sites, this time is termed as an equilibrium time, which represents the utmost adsorption capacity of the adsorbate on the adsorbent [56].

1.6.4.4 The pH of Solution

In the adsorption process, the pH factor is incredibly significant for dye adsorption. A pH media can regulate the degree of electrostatic charges that induced by ionized dye molecules, leading to an adsorption rate that varies with the pH of the medium used. Due to the decreases of positive charge at the interface, the removal of cationic dye at high pH increases. Also, the increase at lower Ph of the adsorption of anionic dye due the increase in positive charge at the interface to electric charge increase within the solution interface, the rises in anionic dye adsorption at lower pH due to the adsorbent surface tends to be positively charged [61].

1.6.4.5 Temperature

For the study of adsorption, temperature is a crucial parameter, because the temperature of waste water fluctuates [71]. Since the foremost dyes adsorption system is exothermic, the temperature greatly affects the number of adsorbed species. In accordance with the speculation of Henry Le Chatelier, higher temperature activity of the exothermic process prefers conditions that develop less heat. As a result, the number of adsorbate adsorbed at the equilibrium decreases with increasing temperature at a given pressure [77].

Temperature thus greatly affects the equilibrium condition of the adsorption mechanism and changes the parameters of thermodynamics. Regulation the temperature of the system regulates the adsorption rate of the contaminant. The adsorption rate of endothermic reactions and desorption rates of exothermic reactions could be increased by high temperatures [62].

Chapter Two:

Literature Review

2.1 Related Adsorption Studies in Literature Review

2.1.1 Results of Some Studies that are Associated with BPB Dye Adsorption

Due to its ease, simple design, high performance and extensive application, adsorption is one in all the most methods for water treatment [59]. The researchers therefore develop low-cost environmentally safe adsorbents for full-scale dye treatment [56]. In table 8 are some results provided by using different adsorbents for BPB removal from wastewater.

Table 8. *The value of adsorption capacity* $q_{m\ (mg/g)}$ *of some adsorbent for the removal of BPB dye.*

Adsorbent name	$\boldsymbol{q_m(mg/g)}$	**Reference**
α-Chitin nanoparticles	22.72	[61]
Activated charcoal	5.0×10^{-2}	[66]
SiO_2 .Bth^+ .$PF6^-$ ionic liquids	238.1	[61]
Modified layered silicate	184.5	[44]
Sorel's cement nanoparticles	4.88	[44]
Polymer-clay composite	About 7.5	[65]
Mesoporous MgO nanoparticles	40	[78]
Mesoporous hybrid gel	18.43	[79]
Graphene oxide functionalized magnetic chitosan composite	10	[70]
Iron oxide nanoparticles	About 110	[77]
Fe_2O_3 -ZnO-$ZnFe_2O_4$/carbon nanocomposite	90.91	[80]
Fe_3O_4/MIL-88A	141.9 - 167.2	[44]

2.1.2 Results of Some Studies that are Related of Using Select Adsorption of Various Class of Dye

Lately, innovations within the nanoscience and nanotechnology have proposed that the employment of the many promising nanomaterials could address or substantially reduce several environmental issues including waste water treatment. The variety of nanomaterials with unique features, like nano-adsorbents that have proven effective in the removal of pollutants from manufacturing, domestic and agricultural waste. Variety of studies show on the role of move into the active adsorption of organic dyes [62]. In the table 9, a number of results are mentioned as within the literature reviews:

Table 9. *Comparison of the most adsorption capacity* $q_{m\,(mg/g)}$ *of a number of dyes on GO.*

Adsorbent	**Name of dye**	$q_m(mg/g)$	**Conditions**	**Reference**
GO	Methylene blue (MB)	244	pH=6, t=5 hr, T= 25 °C	[61]
GO	Methyl orange (MO)	37.2	pH=3.9, t=20 min, T=30	[81]
GO	Crystal violet (CV)	207.4	pH=3.9, t=40-60, T=30	[81]

2.2 Strategies of Study

According to previous studies, graphene oxide has several advantages and properties that are related their use as an efficient and promising adsorbent for water treatment. In this study, graphene oxide in two different size distributions with two different lateral sizes (450 nm and 200 nm) were synthesized and used as adsorbent for removal of BPB dye. GO-450 nm was prepared by oxidation–reduction reaction (Hummers method), followed by using tip sonicator to convert part of it GO-200 nm. FTIR spectroscopy and Scanning electron microscopy (SEM) techniques were used to characterize the GO nanosheets. The effect of several parameters as pH, adsorbent dose, contact time and temperature on the removal of BPB dye by graphene oxide nano sheets was investigated.

Chapter Three:

Methodology

3.1 Materials and Methods

In this chapter, the materials and instruments that are used for synthesis and characterization of both the GO-450 nm and GO-200 nm will be illustrated. Moreover, the procedure of BPB dye removal by batch adsorption will be described.

3.1.1 Chemicals

Graphite powder < 20µm, BPB sodium salt powder, and potassium permanganate (99%), were obtained from Sigma Aldrich and used further without purification. Sulfuric acid (95%), nitric acid (70%), hydrochloric acid (32%), sodium chloride (99.9%), hydrogen peroxide (30%), sodium hydroxide (99%) were all technical grade and used as received.

3.1.2 The Instrumentation

FT-IR spectrometer by Perkin-Elmer with a range of (4000–400 cm-1) for spectroscopic analysis. The morphology and particle size of GO samples were analyzed by scanning electron microscopy (FEI Nova Nano SEM 200 with an accelerating voltage of 15 kV) at Leibniz Institute for Solid State and Materials (Germany). To reduce the size of GO, the ultrasonic processors Sonics, Materials VC-750-220, Fisher Scientific was used. UV/Visible spectrophotometer (JENWAY 7205, with 1.0 cm quartz cell) is used to characterize the concentration measurement of BPB dye. Other instruments include a pH meter, air orbital shaker (SEA*STAR NO.61010-1) and set for suction filtration were used.

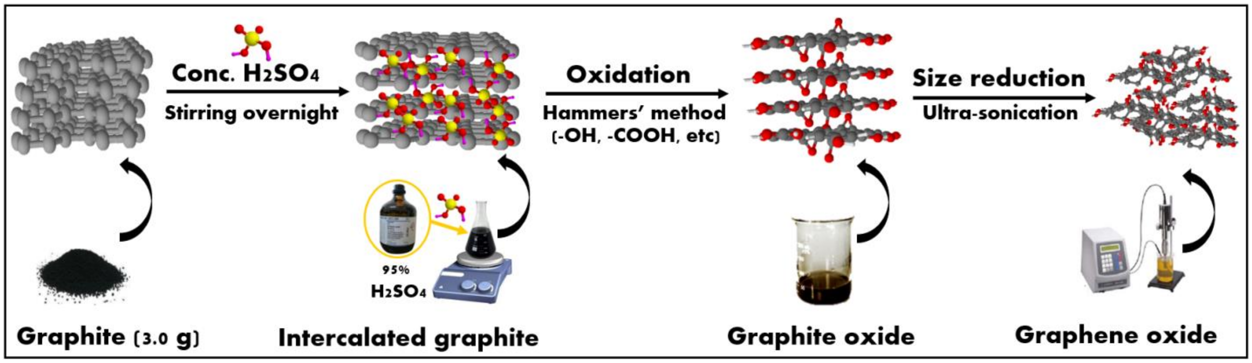
3.2 Methods

3.2.1 Synthesis of GO and the Reduced Size of GO

GO was synthesized by a modified Hummers-Offeman method [82]. Briefly, 3.0 g of graphite and 150 g NaCl were mixed and grounded in mortar for 20 min, the ground graphite was dissolved in warm distilled water at 45°C then collected using double ring filter paper by suction filtration. The filtered graphite placed in 69 ml (96 %) H_2SO_4 and left overnight. Thereafter, the flask placed in next step is placed in an ice bath to reduce the reaction temperature below 10°C. Subsequently, 9.0 g of $KMnO_4$ was added slowly to the suspension over 3 hours with continuous stirring. After complete addition of the $KMnO_4$, the temperature was raised to 35°C and stirred for 30 min and 45 min at 50 °C. The suspension became pasty and brownish in color. Thereafter, with continuous stirring for 45 min a 138 ml of distilled water was added slowly added into the solution and the temperature maintained at degree below boiling point. The suspension was treated by adding 420 ml distilled water and 30 ml H_2O_2 (32%). The product was filtered and washed 5 times with HCl (5%) and distilled water, then centrifuged for 60 min at 6000 rpm. The final product (graphite oxide) was filtered and dried in an oven at 50°C for 2 hrs. [83, 84].

Preparation of GO reduced size

1.0 mg/ml of graphite oxide was sonicated in an ultra-sonic bath for 30 min under controlled power and time to produce a reduced size of GO [85]. The details of this step are represented in scheme 3.



Scheme 3. Formation of graphene oxide using the tip sonicator.

3.2.2 Preparation of Dye Solution

The stock solution of BPB dye (1000 ppm) was prepared by weighing 1.0 g of BPB powder then dissolved in 1000 ml of distilled water. Experimental batch solutions of the required concentrations (10, 30, 50 and 75 ppm) were prepared by dilutions from the stock solution. Thereafter, the calibration curve was fitted according the absorbance values at λ_max that was 457 nm of the series BPB dye (5, 10, 15, 20, 30) using UV/Visible spectrophotometer. Figure 5 shows the color intensity of the BPB series concentration at pH 2 and 4, respectively.

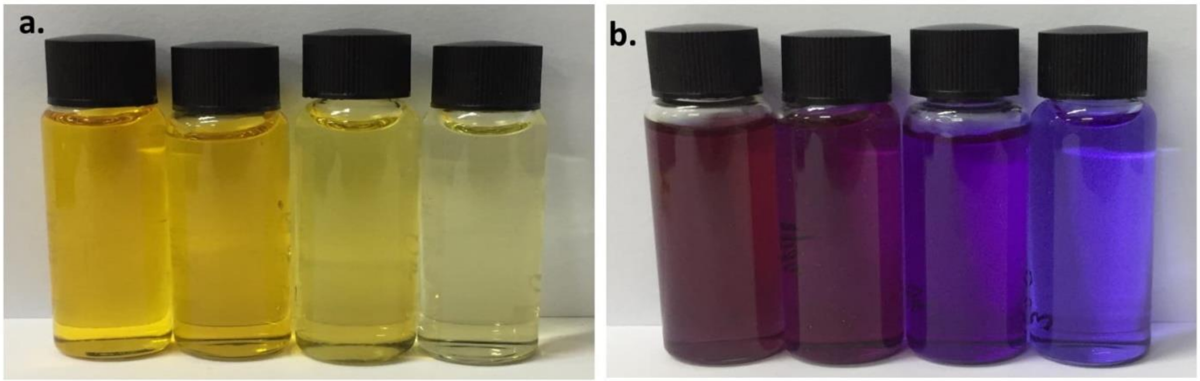


Figure 5. Different concentrations of BPB dye (a) at pH=2, (b) at pH=4.

3.2.3 Batch Studies

Batch adsorption experiments were achieved in an orbital shaker (SEA*STAR NO.61010-1) at a constant shaking rate 210 rpm. The effect of adsorbent dose, contact time, solution pH, initial concentration and temperature were studied. A 100 ml of dye solution of known concentrations were placed in 100 ml covered conical flask with known mass of GO. Values of pH were regulated using 0.1 M of HNO_3 or 0.1 M of NaOH solutions, at various mixing time and temperature range. Separation of the solid phase from liquid phase at different time was achieved by using suction filtration followed by measuring the residual dye concentration using UV-Visible spectrophotometer.

3.2.3.1 Influence of pH on the Adsorption Process

The effect of pH on BPB dye adsorption were studied from 2 to 10. The test was done by adding 100 ml of 10 ppm of BPB dye solution in conical flasks. After pH adjusting, 160 mg of every GO and reduced size of GO are added to the tested solution, they were placed in an air orbital shaker at 210 rpm agitation speed, for 40 minutes of contact at the constant temperature of 25 °C. After that 5 ml of every sample was filtered by suction filtration and the residual amounts of BPB dye were determined by measuring the absorbance at different pH values.

3.2.3.2 Influence of adsorbent dose

The initial concentration of BPB dye used in this section was maintained at 10 ppm and the volume of solution 100 ml. The pH was set for the appropriate value of adsorption process that decided in the previous section. Different amounts of adsorbents 20, 40, 80, 160, 320 and 480 mg were added to those solutions and kept for 40 minutes of contact time, at 25 °C and agitation speed of 210 rpm.

The residual amount of BPB dye concentrations at each adsorbent dose were analyzed using UV-Visible spectroscopy by measuring the absorbance at 457 nm.

3.2.3.3 Influence of Contact Time

The effect of contact time was studied by taking different initial concentrations of dye solutions (100 ml) mixed separately with 160 mg GO at 25°C. The pH remained constant as previously described. The batch samples were agitated at 210 rpm for 10, 20, 40, 60, 100 and 120 min. After each time interval, the solid materials were filtrated and followed by measuring the amount of unreacted BPB at 457 nm.

3.2.3.4 Influence of Initial Dye Concentration

The batch adsorption study in this section was carried out to investigate the adsorption isotherms, by using 100 ml of various initial BPB dye concentrations 10, 30, 40 and 75 ppm keeping all other variables at fixed values. These values as pH, adsorbents dose, contact time and the agitation speed were obtained from optimum conditions reached from previous steps. All experiments were carried out room temperature. Samples were filtered and the absorbance of remaining BPB dye was measured at 457 nm.

3.2.3.5 Influence of Temperature

To understand the effect of temperature on the removal of BPB dye from the batch solution, adsorption experiments were performed at different temperatures. Different samples with an initial BPB dye of 10 ppm were prepared, and their pH were adjusted to a fixed value, followed by adding 160 g of GO-450 nm and GO-200 nm, at constant agitation speed of 210 rpm and contact time of 40 minutes. The kinetic studies were performed at three values of temperature (298K, 318K and

338K). The remaining BPB dye concentration after filtration was evaluated using spectrophotometer by measuring the absorbance at 457 nm.

Chapter Four:

Results and Discussion

4. Results and Discussion

4.1 Adsorbent Characterization

Various characterization techniques were used to study the surface of GO adsorbent and to monitor the quality of adsorption process. Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FT-IR) are the two characterization techniques that have been carried out in the present study.

4.1.1 Scanning Electron Microscopy (SEM)

The surface morphology and lateral size of the GO nanosheet were analyzed by scanning electron microscopy (SEM) [84, 86], as shown in figure 6, SEM exhibits two sizes of graphene oxide nanosheet; the average size (lateral width) of prepared GO sheet is approximately 450 nm figure 6(a). However, by using a tip sonicator, the average size of GO particles after sonication is reduced to about 200 nm as shown in figure 6(b). The statistical analyses of GO particles deduced from SEM images are represented in figure 6(c).

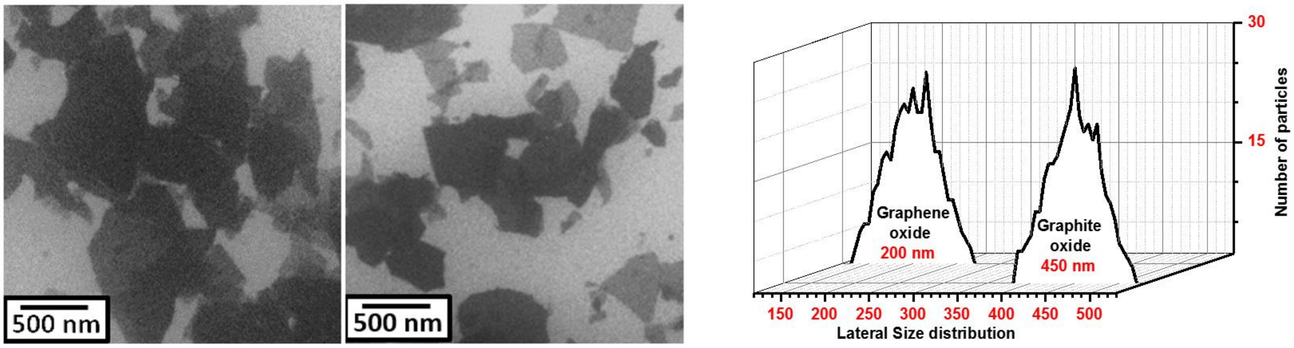


Figure 6. *SEM images of (a) GO-450 nm and (b) 200 nm. (c) is the average width (nm) of GO particles deduced from SEM image, size distribution of GO-450 ± 35nm, GO-200 ± 20nm.*

4.1.2 Fourier Transform Infrared Spectroscopy

FTIR is an important method used to exhibit the characteristic functional groups of GO nanosheets, as well as it shows the interaction between adsorbent and adsorbate throughout the shift in the main peaks of adsorbent [87]. The structures of graphite and graphite oxide (GO-450 nm) were analyzed by this method. In the region of IR from 4000 cm^{-1} to 500 cm^{-1}, the graphite spectrum displays no significant bands, while the FT-IR spectrum of GO indicates the presence of several functional groups on the surface of GO structure as shown in figure 7(a). The broad band at 3312 cm^{-1} represents the stretching vibration of (-OH) due to hydroxyl group in carboxylic and alcohol groups. The significant peak at 1612 cm^{-1} belongs to the double bond (C=C) on the basal plan of graphene sheets. The peak appeared at 1730 cm^{-1} is due to (C=O) group. The weak band in the region of 1231 cm^{-1} is assigned to vibration of epoxide group (C-O), and the peak at 1077 cm^{-1} is attributed to alkoxy group (C-O-C) [87, 88]. The IR spectra of BPB dye as free compound and GO-BPB dye are shown in figure 7(b). According to the IR spectrum of the BPB dye, the peaks observed were at 3250 cm^{-1} corresponding to the (-OH), 1600 cm^{-1} corresponding to the cyclic alkene (C=C) on the structure of BPB dye, 1300 cm^{-1} corresponding to the sulfone group, 1200 cm^{-1} (C-O), 700 cm^{-1} corresponding to the (C-H) group, 616 cm^{-1} corresponding to (C-Br) group. After the adsorption of BPB dye on the GO nanosheets, the peak was spotted at 3106 cm^{-1} corresponding to stretching vibration of (-OH) group. In addition to, shift was observed at 1593 cm^{-1} and 1726 cm^{-1} corresponding to (-C=C-) and (C=O) groups, respectively. Moreover, it was noticed that an increase of both previous peaks that indicate to the adsorption by electrostatic interaction between GO and BPB dye. Both epoxide group (C-O) and alkoxy group (C-O-C) shifted to the 1409 cm^{-1} and 1247 cm^{-1}, respectively. calibration curve of BPB dye, the λ max was

457 nm. Measurements were carried out at pH=2 due to the maximum adsorption capacity at this point.

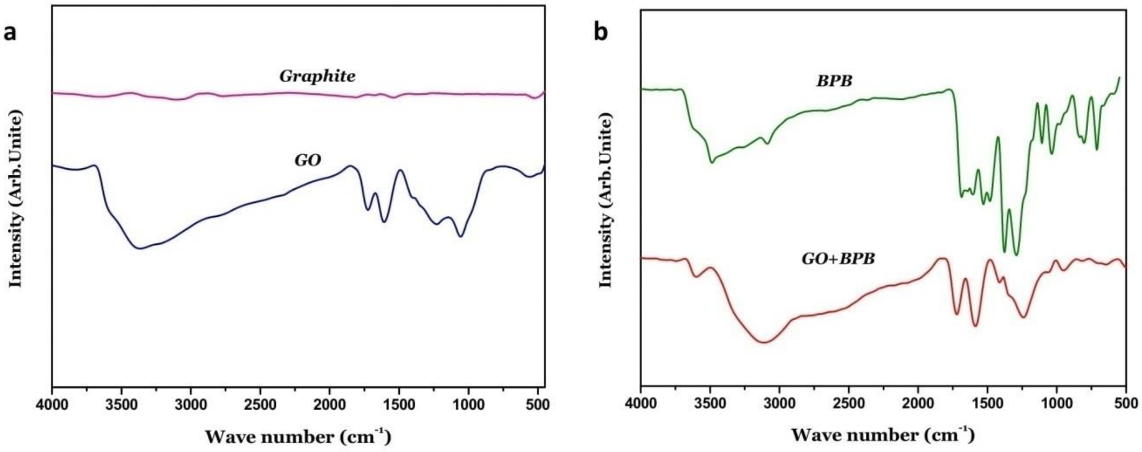


Figure 7. *FT-IR spectra of (a) graphite and the synthesized GO-450, (b)BPB dye and GO-BPB.*

4.2 Characterization of BPB Dye (Adsorbate) by UV-visible Spectrophotometer

The UV-visible spectrophotometer is a method used to measure the absorbance versus specific λ max of analyte. A series of BPB dye concentrations were measured and calibration curve was fitted by using range from 5 to 30 ppm of BPB dye, thereafter the calibration curve was employed to determine the residual amount of BPB dye after adsorption process. figure 8 shows the calibration curve of BPB dye, the λ max was 457 nm. Measurements were carried out at pH=2 due to the maximum adsorption capacity at this point

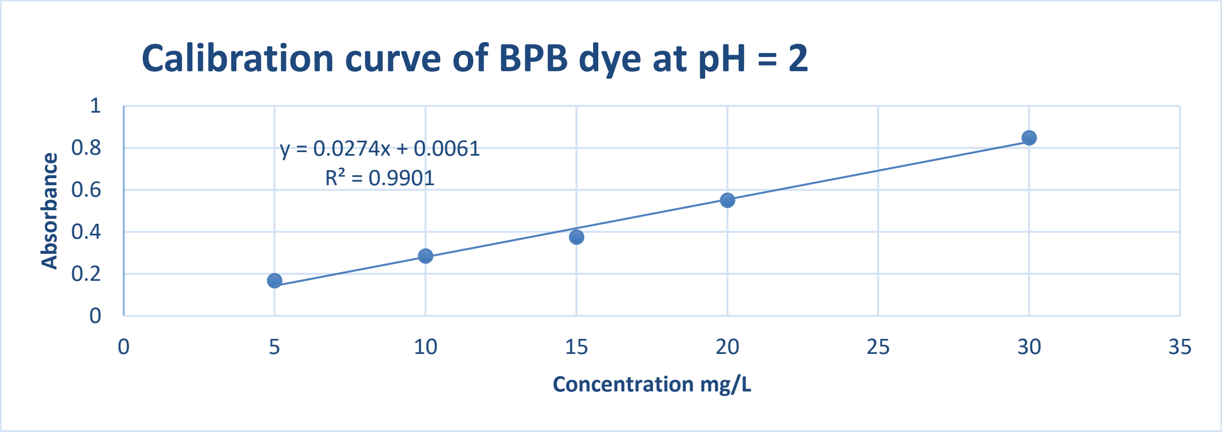


Figure 8. The calibration curve of BPB in acidic media, pH=2.

4.3 Determination of Adsorption

4.3.1 Adsorption Capacity

Values of adsorption capacity (q_e,mg/g) of GO-450 nm and GO-200 nm at different time intervals and BPB concentrations are shown in figure 9. From this figure it is clear that the adsorption capacity increases with increasing the initial concentration of BPB dye on the two size of GO sheets. Obviously, by increasing the concentration of BPB dye, the ratio between the dye molecules to the vacant sites is increasing until the adsorbent surfaces are fully covered [87]. In addition to that, the GO-200 nm sheets show larger value of adsorption capacity than GO-450 nm, and this behavior is attributed to the increase in the surface area of GO-200 nm compared to GO-450 nm.

In the figure 9(a), the adsorption capacity of GO-450 nm with BPB dye of different concentrations and time intervals shows a linear relation at room temperature and pH 2. At low concentration of BPB, the capacity remained no change at different time intervals. In GO 200 nm, the adsorption capacity approximately remains constant at the time intervals from 20 to 120 min under the same conditions as shown in figure 9(b). That behavior is related to the increase in the surfaces area of

GO-200 nm; thus, a massive number of vacant sites are available to rapidly adsorb the BPB from the solution

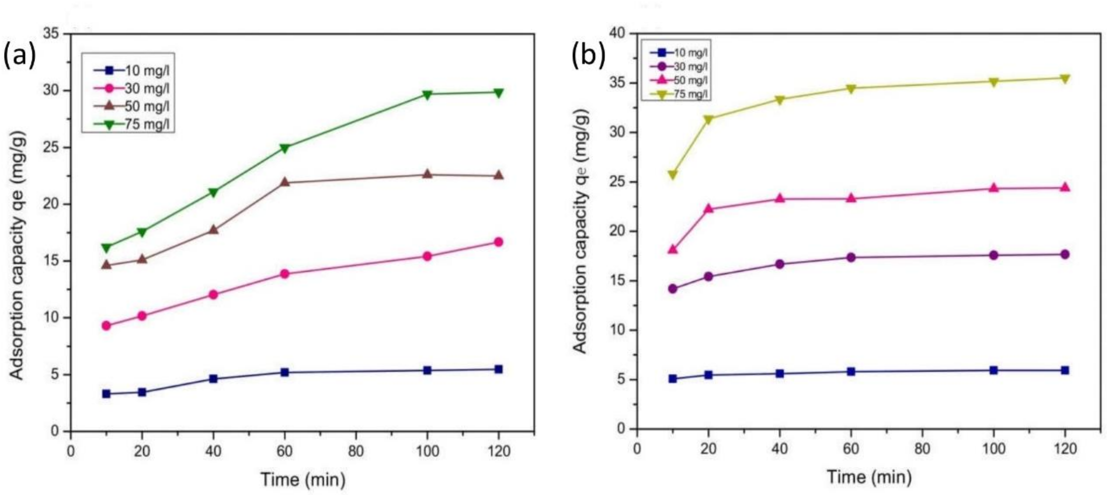


Figure 9. *(a) Adsorption capacity versus time GO-450 nm and (b) GO-200 nm for different BPB dye concentrations and at room temperature.*

4.3.2 Percent Removal of BPB Dye at Different Concentrations and Time Intervals

The percent removal of BPB dye decreased with increasing the concentration of dye as shown in figure10. This behavior is a consequence of the presence of large amount of dye molecules at higher concentrations competing to be adsorbed on a limited number of avilable vacent site on the GO nanosheets [89]. In the same context, the percentage of dye removal was rapid up to 60 min after that the percent removal reached plateau values as shown in panel (a) figure 10.

In panel b figure 10, the percent removal of BPB dye on GO-200 nm shows a rapid removal in the time interval from 10 to 20 min, this result is attributed to an increase in the adsorption sites of GO-200 nm comparing with the sites distributed onto GO-450 nm [90].

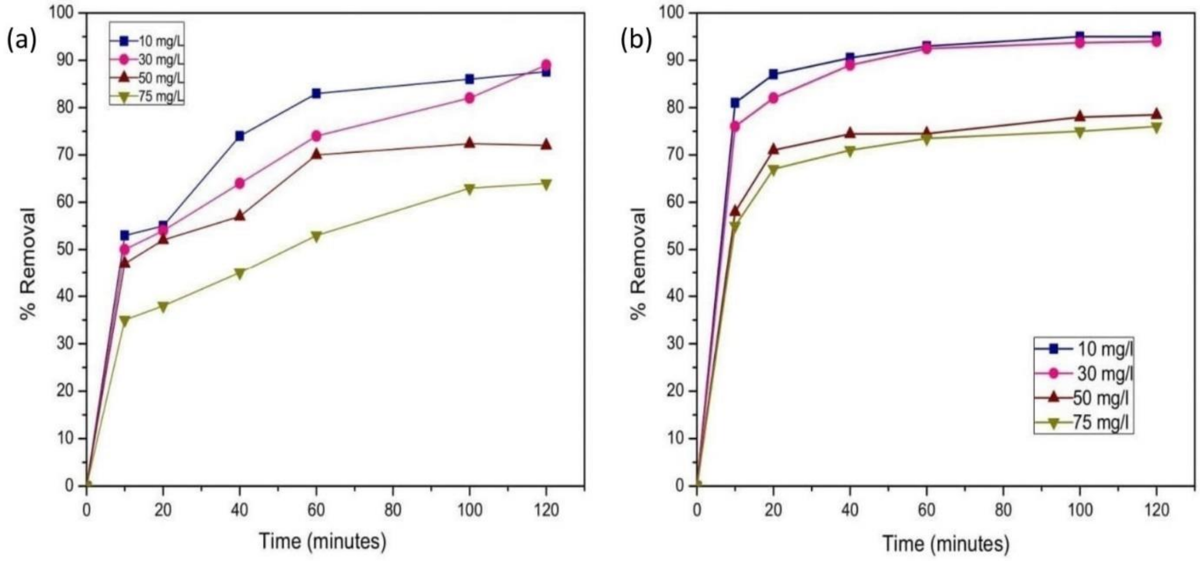


Figure 10. (a) The percent removal of BPB onto GO-450 nm and (b) GO-200nm at different time, dye concentrations and at room temperature.

4.3.3 Adsorption at Different Variables

4.3.3.1 Effect of pH

The pH factor is a critical factor in the adsorption mechanism between the BPB dye and the GO adsorbent. The change in pH has dual effects on both adsorbent and adsorbate; in one hand the pH changes the degree ionization and hence the charges on GO which acts as the adsorbent [56]. On other hand, BPB dye is an acid- base indicator, thus the degree of ionization of the functional groups of BPB dye is also affected by pH change.

BPB acts as weak acid-base system (HIn/In⁻), where HIn form has a different color than the In⁻form in the aqueous solutions. HIn form of BPB dye absorbs red light and transmits blue color, and therefore, the solution of dye is blue. At low pH the (In⁻) form of BPB dye absorbs ultraviolet light and transmits yellow in solution, so the solution of dye appears in yellow color. In pH range of 3.0 and 4.6, BPB dye acts as an acid-base indicator. The color switches from yellow at pH 3 or less to blue at pH 4.6 or more, and this change is a reversible reaction which is shown in figure 11.

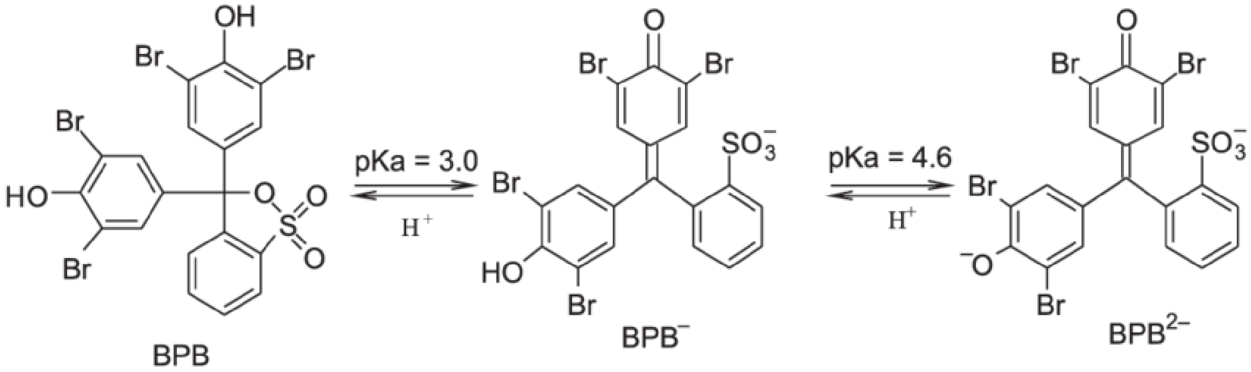


Figure 11. *Dissociation equilibrium of BPB dye in different pH media.*

The aqueous solution of an acid base indicator goes over a color transition within a narrow pH range, ΔpH = 2. Therefore, the best way to study the pH factor on the adsorption process of BPB dye is to set different calibration curves of BPB dye at different pH media to deal with this case of color transition. The first calibration curve represents the dye in acidic media shown in figure 12(a), and the second calibration curve was fitted at pH= 4 shown in figure 12(b). The third calibration curve was fitted at pH=6 as in figure 12(c). The last calibration curve was adjusted at pH= 8 as in figure 10(d).

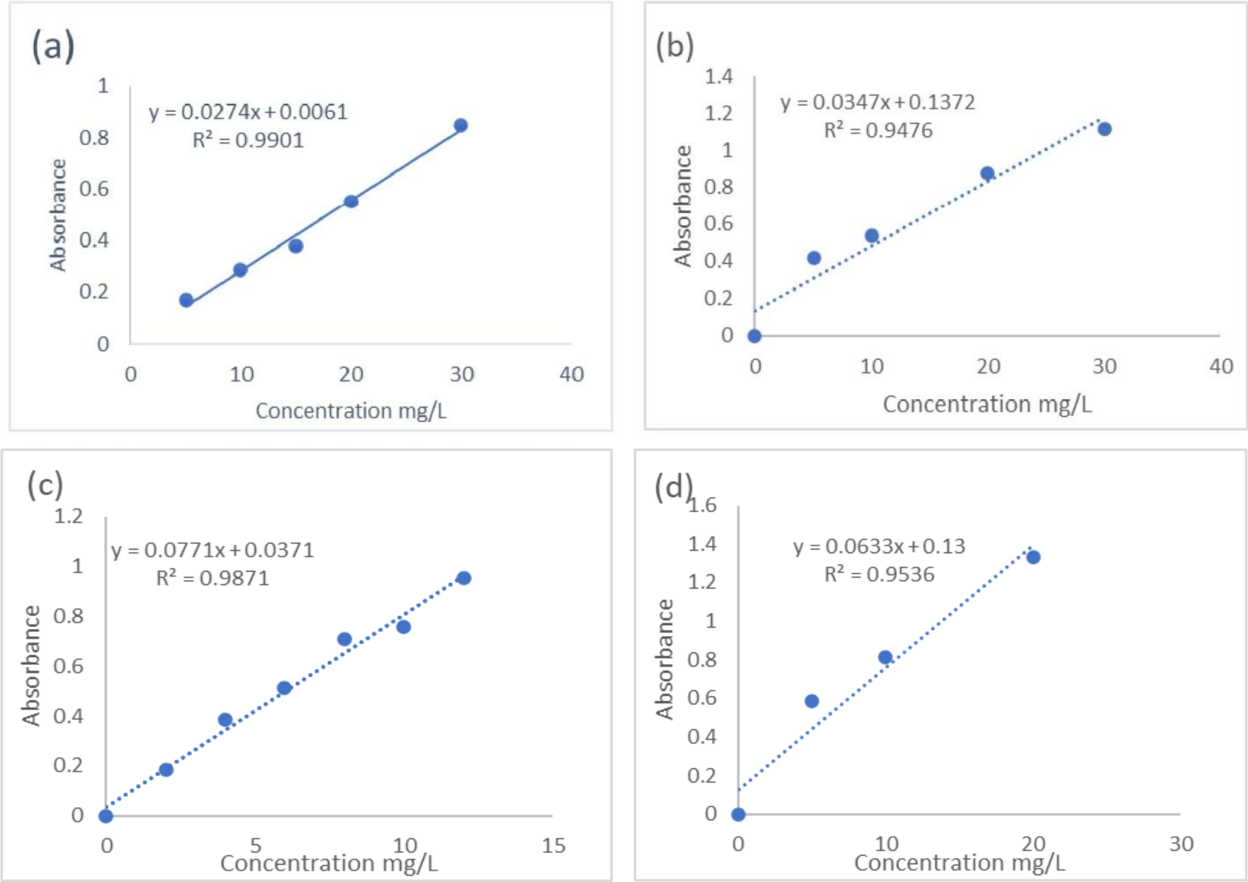


Figure 12. *Calibration curves of BPB dye at different pH media, (a) at pH=2, (b) at pH = 4, (c) at pH = 6, (d) at pH = (8-10).*

Figure 13 shows the effect of pH on the adsorption of BPB dye on GO-450 nm andGO-200 nm. The maximum percentage removal of dye was at pH= 2, but beyond this point a decreasing trend was followed with an increase in pH of the solution. At high pH, the surface of GO adsorbents becomes more negatively charged due to the deprotonation of the oxygen groups that are located on the surface of GO, and the predominant form of the dye in basic media (In^{-}). Therefore, a more repulsive forces between the BPB dye and GO sheets is expected, and as a result decrease in the removal of BPB dye from the batch solution [76]. Furthermore, as the solution becomes more acidic, adsorption of dye shows an increasing trend. This can be attributed to three types of interactions between BPB dye and the adsorbent at lower pH. First, π-π interaction between the aromatic ring of dye and benzene rings of GO. Second, hydrogen bonding between -COOH and -OH groups of GO and -OH groups of the dye. The third type, electrostatic attraction between an anionic dye and the positive charge of GO at low pH [70]. In addition, the GO–200 nm shows higher removal comparing with GO–450 nm, and this effect is due to the increase of the surfaces available for adsorption.

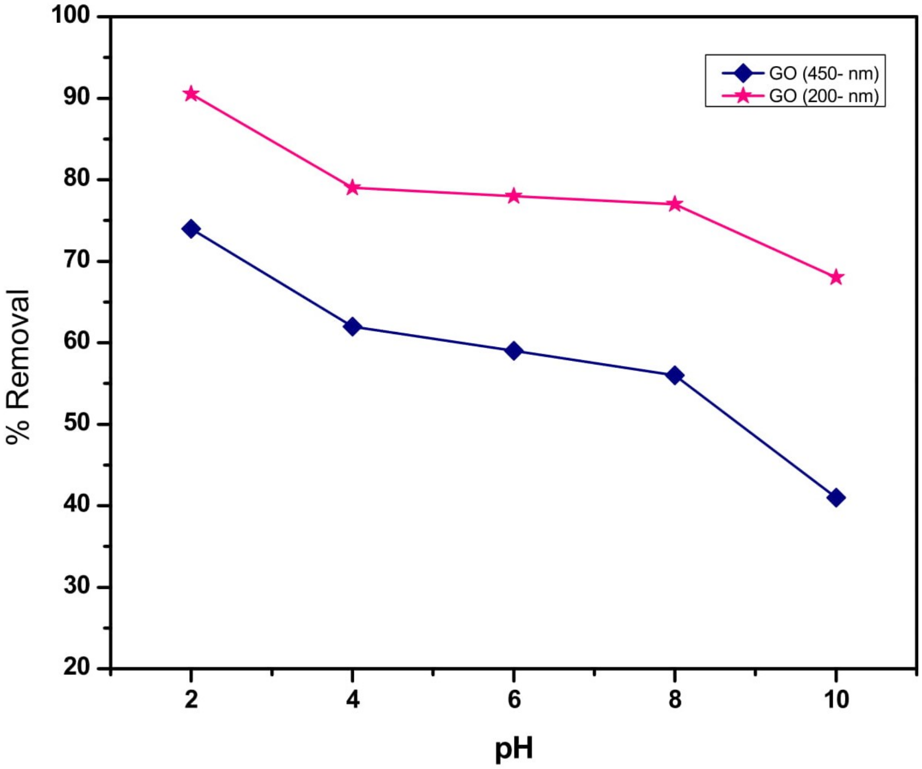


Figure 13. Effect of pH on the removal of BPB dye, BPB concentration=10 ppm, at room temperature.

4.3.3.2 Effect of adsorbent dose

The percentage of BPB dye absorbed at different amounts of GO-450 nm were studied and the results are shown in figure14. The trend of the graph shows an increase in the percentage of BPB dye adsorbed as the adsorbent dose was increased from 25.0 to 475.0 mg. This referred to an increase in the contact surface area of adsorbent which means the availability of adsorption sites was increased, thus the percent removal of BPB dye was also increased [81]. For both GO-450 nm and GO-200 nm, the optimal adsorbent dose was found to be 160 mg. after this dose the adsorbent surface became saturated, so the residual dye ratio in aqueous solution nearly was constant.

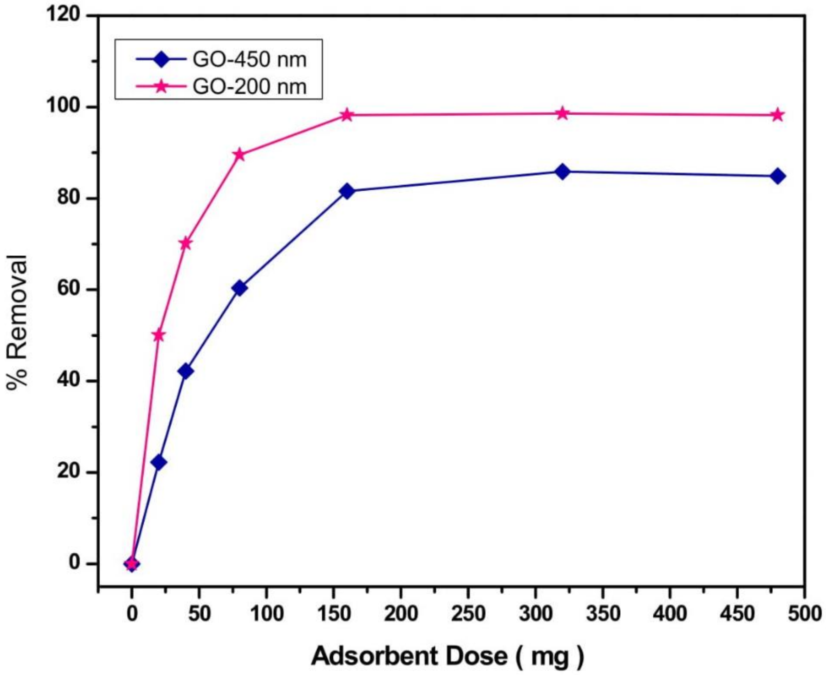


Figure 14. *Effect of adsorbent dose (BPB dye concentration= 10 ppm, pH= 2, contact time = 40 minutes, at room temperature).*

4.3.4 Adsorption Isotherm Models

Adsorption isotherms are often referred to as equilibrium data that assess the adsorbent's ability to remove the adsorbate and may indicate the types of adsorbate layer that formed on the adsorbent surface [44, 81]. In this study two models of isotherm were used, the Langmuir isotherm (equation 3) and Freundlich isotherm (equation 5).

Evaluation of the experimental data using Langmuir and Freundlich isotherms are shown in figure 15 and 16 for both GO-450 and GO-200 nm, respectively. The linear relation of Langmuir was tested by a plot of C_e/q_eversus BPB dye equilibrium concentrations. From the graph, values of q_m (maximum adsorption capacity) and K_l (Langmuir constant) were calculated. In the Freundlich isotherms a linear plot of $\ln q_e$versus $\ln C_e$, enables the determination of the constants n and K_f. The value of n is used to predict the heterogeneity of the adsorbent and the intensity of the adsorption while K_f (Freundlich constant) is related to the adsorption capacity [44, 72].

The isotherm constants and the correlation coefficients (R^2) of both models are listed in table 10 and table 11 for the adsorption of BPB dye on the two sizes of GO-450 nm and 200 nm. Depending on the tables, there are slightly an increase in q_m value between GO-450 nm and GO-200 nm, also an increase the value of q_m over an increasing in the equilibrium concentration. Moreover, the values of R_L which was defined by equation 4 are ranged from (0 to 1), and revealing that the adsorption of BPB on GO is a favorable process. From table 10 and 11, it is noticed that the values of n are bigger than 1, reflecting the favorable adsorption. In addition to an increase in the time of interval, the value of Freundlich isotherm parameter K_f has been determined to increase [73].

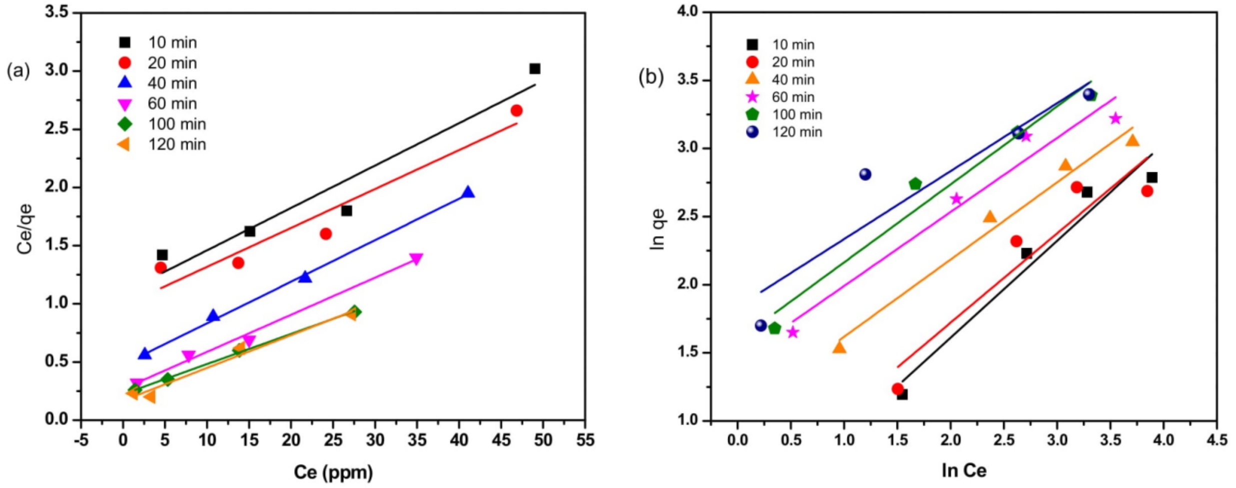


Figure 15. *Adsorption isotherms of BPB dye on GO-450nm at room temperature, (a): Langmuir, (b): Freundlich.*

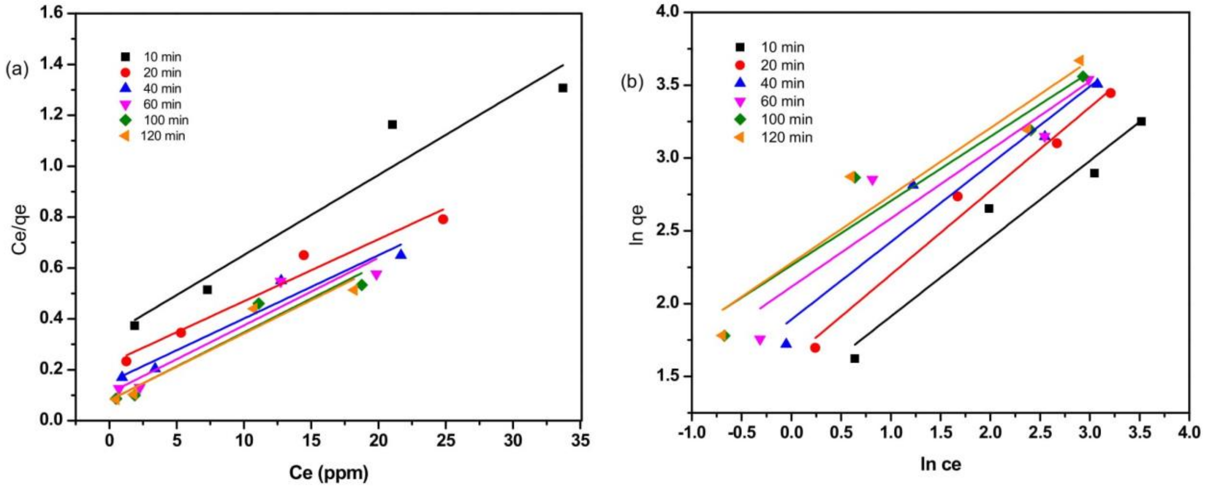


Figure 16. *Adsorption isotherms of BPB dye on GO-200nm at room temperature, (a): Langmuir, (b): Freundlich.*

Table 10. *Langmuir and Freundlich parameters for the adsorption of the BPB onto GO-450 nm at room temperature.*

Time (min)	**Langmuir isotherm**				**Freundlich isotherm**		
	q_m (mg. g^{1})	K_L (L.mg^{-1})	R_L	R^2	K_F	n	R^2
10	27.8	0.033	0.287	0.89	1.21	1.41	0.928
20	29.4	0.034	0.28	0.89	1.51	1.52	0.823
40	28.57	0.074	0.153	0.997	2.86	1.76	0.968
60	31.25	0.119	0.101	0.988	4.25	1.84	0.937
100	38.46	0.116	0.103	0.997	4.9	1.75	0.946
120	35.7	0.167	0.074	0.963	6.28	2.00	0.809

Table 11. *Langmuir and Freundlich parameters for the adsorption of the BPB onto GO-200 nm at room temperature.*

Time (min)	**Langmuir isotherm**				**Freundlich isotherm**		
	q_m (mg. g^{1})	K_L (L.mg^{-1})	R_L	R^2	K_F	n	R^2
10	32.26	0.09	0.129	0.92	3.963	1.873	0.932
20	41.667	0.107	0.112	0.945	5.078	1.739	0.973
40	40	0.16	0.077	0.92	6.626	1.876	0.912
60	37.04	0.25	0.051	0.88	8.289	2.128	0.832
100	37.04	0.34	0.038	0.91	9.612	2.262	0.867
120	38.46	0.33	0.038	0.911	9.757	2.155	0.87

As a result of linear correlation coefficient values (R^2) of both isotherm models in this study, it is found that the Langmuir model fits the data better than the Freundlich model, which indicates that the adsorption of BPB onto GO is a type of monolayer adsorption. Furthermore, the maximum monolayer adsorption capacities at optimum time calculated from Langmuir isotherm were 28.57 mg/g and 40 mg/g for GO-450 nm and GO-200 nm GO, respectively.

4.3.5 Adsorption Kinetic Study

In order to demonstrate the adsorption kinetic of BPB dye onto GO, the experimental data was verified by the Lagergren's pseudo-first-order model (PFO) and Ho's pseudo-second-order model (PSO), that were represented by equation 6 and 8 (see section 2.2.2), respectively. Figure 17 and 18 show the linearized plot of the PFO model and PSO model for both GO-450nm and GO-200nm. The results of kinetic parameters were calculated by plotting the slope and intercept value of both models, they are sorted in table 12 and 13.

The models with the highest regression coefficient (R^2) have been considered the best model to explain the kinetics of experimental BPB dye adsorption. From the data obtained, the values of regression coefficients (R^2) of PSO model are higher than that of PFO. In addition to that, the values of calculated capacities (q_e cal.= 3.177 and 1.68) from the PFO model for GO-450 nm and GO-200nm are not consistent with the experimental values *(*q_e exp. = 5.48 and 5.94). On the other hand, the values of calculated capacities ($q_e$cal.) from the PSO model are very closed to the experimental values ($q_e$exp. = 5.988 and 6.061). Based on the results of the experimental data of the BPB dye adsorption on GO-450 nm and GO-200 nm it could be explained correctly by PSO kinetic model [89].

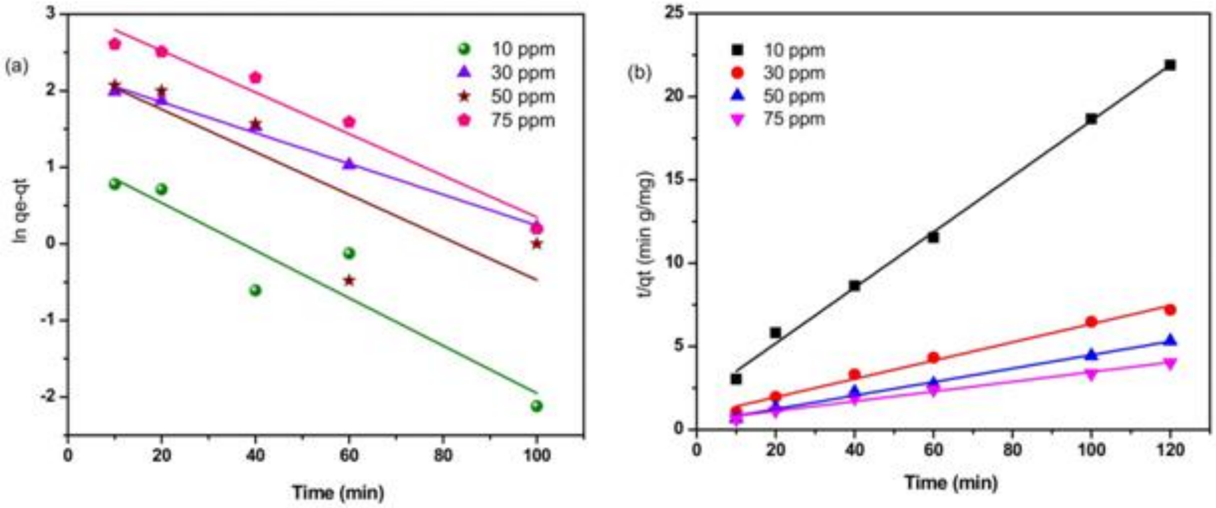


Figure 17. *Pseudo-first order (a) and Pseudo-second order (b) kinetic adsorption model of BPB on GO-450 nm at room temperature.*

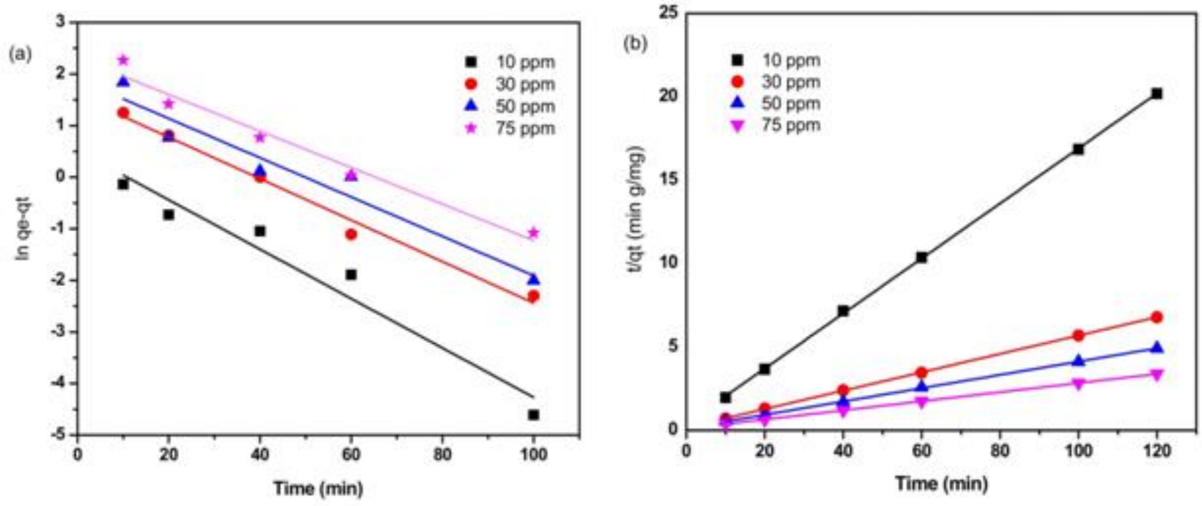


Figure 18. *Pseudo-first order (a) and Pseudo-second order (b) kinetic adsorption model of BPB on GO-200 nm at room temperature.*

Table 12. *Pseudo-first order and pseudo-second order parameters for the adsorption of the BPB onto GO-450 nm at room temperature.*

C_i mg/l	**$q_{e,exp}$ mg/g**	**Pseudo first- order**			**Pseudo-second order**		
		K_1 $\min^{-1}$	$q_{e,cal}$ mg/g	R^2	K_2 g/mg. min	$q_{e,cal}$ mg/g	R^2
10	5.48	0.013	3.177	0.84	0.013	5.988	0.997
30	16.675	0.02	9.5	0.99	0.0036	18.18	0.987
50	22.5	0.028	10.115	0.604	0.004	24.39	0.993
75	29.88	0.047	36.89	0.884	0.0016	34.48	0.985

Table 13. *Pseudo-first order and pseudo-second order parameters for the adsorption of the BPB onto GO-200nm at room temperature.*

C_i mg/l	**$q_{e,exp}$ mg/g**	**Pseudo first- order**			**Pseudo-second order**		
		K_1 $\min^{-1}$	$q_{e,cal}$ mg/g	R^2	K_2 g/mg. min	$q_{e,cal}$ mg/g	R^2
10	5.94	0.048	1.68	0.938	0.0674	6.061	0.999
30	17.67	0.04	4.85	0.983	0.0174	18.182	0.999
50	24.39	0.045	8.06	0.917	0.011	25.641	0.999
75	35.5	0.035	10.07	0.961	0.0069	37.037	0.999

Table 14. *Kinetic parameters and regression coefficient (R^2) of BPB dye adsorption on GO-450 nm and GO-200 nm.*

Adsorbent	$q_{e,exp}$ **(mg/g)**	**Pseudo-first-order model**			**Pseudo-second-order model**		
		K_1 (1/min)	$q_{e,cal}$ (mg/g)	R^2	K_2(1/min)	$q_{e,cal}$ **(mg/g)**	R^2
GO-450nm	5.48	0.013	3.177	0.84	0.013	5.988	0.997
GO-200nm	5.94	0.048	1.68	0.938	0.0674	6.061	0.999

4.3.6 Effect of Temperature

In most chemical reactions and processes, it is very important to know the effect of changing temperature on the efficiency of adsorption or desorption on a solid surface [71].

The isothermal BPB dye adsorption experiments on GO-450 nm and GO-200 nm at different temperatures (298K, 318K, and 338 K) were studied under optimized conditions. To evaluate the effect of temperature on adsorption process of BPB dye on the GO, thermodynamic parameters such as enthalpy, entropy and Gibbs free energy were obtained by using equation 10 and 11 given in section 2.2.3 and summarized in table 15.

The value of enthalpy (ΔH) and the entropy (ΔS) are calculated from the slope and intercept of the linear regression of $\ln(qe / Ce)$ and $1/T$ (equation 10) as shown in figure 19(a).

Based on the findings of this study, the percent removal of BPB dye decreases with an increasing in temperature and this suggests that the adsorption process is exothermic as shown in figure 19(b) BPB dye may be inclined to move from the solid phase to the bulk solution as the temperature of the solution increases. The solubility of the dye in the solution increases at a higher temperature so the interaction between the dye and adsorbate will be decreased [66]. The negative ΔH value indicates the exothermic existence of the adsorption process. The negative value of ΔS represents the decreased randomness during the adsorption of BPB on GO at the solid/liquid interface. This decrease in randomness is mainly due to the chelating of the BPB dye molecule to the active GO sites to create a stable structure.

The values of ΔG are negative, which is obtained by using equation 10 at different temperature. The negative value means that the adsorption process of GO towards BPB dye is spontaneous. The values of ΔH suggested that adsorption in this work is classified as physisorption [71].

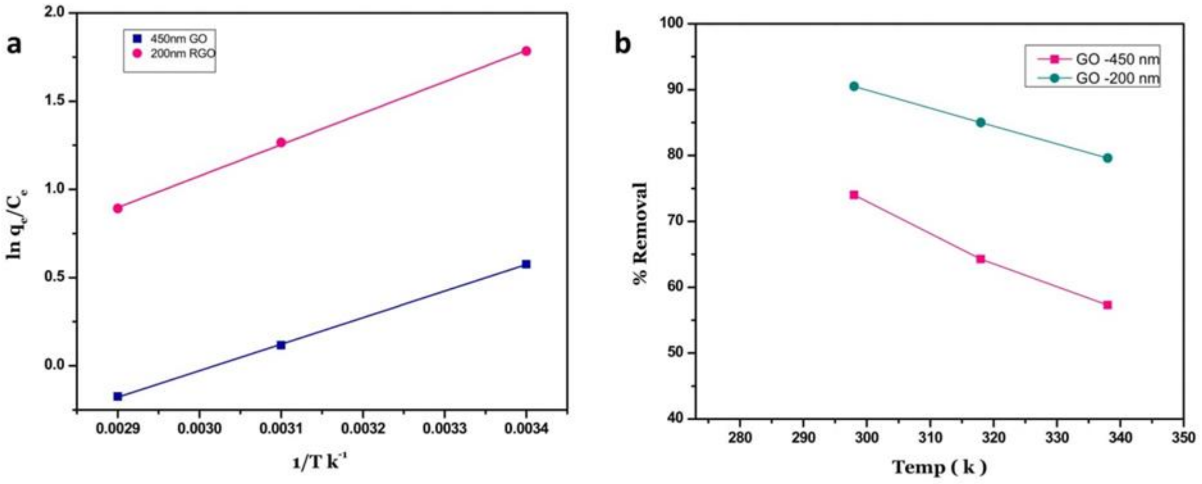


Figure 19. *(a) Van't Hoff for the adsorption of BPB dye on GO -450 nm and GO -200 nm (BPB dye= 10 mg/L), (b) effect of temperature on the percentage removal of BPB dye.*

Table 15. *The thermodynamic parameters for the adsorption of BPB dye on GO-450 nm and GO-200 nm.*

Adsorbent	**ΔH°** **kJ/mol**	**ΔS°** **J/mol.K**	**ΔG at temperature °C** **kJ/mol**		
			25 °C	45°C	65°C
GO-450 nm	-12.497	-37.696	-1.173	-0.413	-0.347
GO-200 nm	-14.81	-35.49	-4.231	-3.521	-2.811

Chapter Five:

Conclusion and Recommendations

5.1 Conclusion

In this work two pore surface size of graphene oxide (GO-450 nm and GO-200) nm were synthesized from graphite and used as starting material for the removal of dye. Dyes are recognized to be the main organic contaminant released to the environment from aqueous solution. The data of this work revealed that the adsorption process was highly affected by pH value, initial BPB dye concentration, contact time and the temperature of reaction. Moreover, because of the high surface to volume ratio, the removal efficiency of BPB dye on the smaller sizes of GO sheets produced was a higher. The maximum adsorption capacity on the GO-200 nm was 40 mg/g and for GO-450 nm was 28.57 after 40 minutes of contact time, using 160 mg of GO adsorbent and at pH = 2. In order to illustrate the isotherms of adsorption process, both Freundlich and Langmuir models were used and Langmuir model provides the best equilibrium data fitting. BPB adsorption kinetics on GO-450 nm and GO-200 nm show that the experimental data can be well fitted by the pseudo-second-order rate. The calculated thermodynamicparameters indicated that the adsorption of BPB was spontaneous in nature and exothermic. Lastly, the adsorption by using GO is considered to be a simple, efficient, flexible and affordable process to remove BPB dye from water.

5.2 Recommendations

Hopefully an additional work on graphene oxide will be decided to carried out in the future. The adsorption process may by enhanced by boosting the functional groups on the surface of graphene oxide. Moreover, we may introduce approved techniques like irradiation by microwaves which are used to regenerate the GO after adsorption process.

The research, on the other hand, includes the most common dyes used locally so GO adsorption work may be used to treat a real sample of a mixture of dyes that contaminate our local water.

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المُلَخّص

تشكل العديد من الأصباغ المصنعة الناتجة عن الانشطة الصناعية تهديدا للبيئة وحمايتها، وفي هذه البحث تَمَّ دراسةِ إزالة صبغة البروموفينول الزرقاء كمثال على الاصباغ المصنعة باستخدامِ جزيئاتِ أكسيدِ الغرافين النانوية، ولهذه الغاية تم تحضير جزيئات أكسيد الغرافين بحجم 450 نانوميتر وتم الإشارة لها اختصارا GO-450 nm، واستخدم جهاز للموجات فوق الصوتية لتحويل الجزيئات السابقة الى جزيئات بحجم 200 نانوميتر وتم تسميتها GO-200 nm، وقد تم التأكد من حجم الجزيئات السابقة من خلال المجهرُ الإلكترونيّ (SEM) والتحاليل الإحصائية. كما اظهر جهاز الطيف بالأشعة تحت الحمراء (FTIR) تكون العديد من المجموعاتِ الفاعلة التي تَحوي ذَرات الأكسجينِ موزعةً على سطحِ جزيئاتِ أكسيدِ الغرافين.

استخدمِ جِهاز الطَيف المَرئي "فوق البنفسجي" UV-visible spectroscopy لدراسة ديناميكا الإدمصاصِ والعَوامِل المُتَحَكِمَة بهذهِ العَملية مثل التركيزِ الابتدائي، ودرجة الحموضة، وَدَرجِة الحَرارَة والزَّمن المتاح لعملية الادمصاص، وقد بينت الدراسة ان نموذج لانغمير هو الأكثر ملائمة للنتائج التي تم الحصول عليها كما ان سعةُ الادمصاص لجزيئاتِ أكسيدِ الغرافين زادت بصورة ملحوظة من 28.57 ملغم/غم في حال استخدام GO-450 nm إلى 40 ملغم/غم عند استخدام GO-200 nm ويمكن تفسير هذه الزيادة في الفاعلية الى الزيادة في مساحة السطح المتاح لعملية الادمصاص في الجزيئات الأصغر حجما. اما دراسة حركية عملية الادمصاص فبينت ان هذه العملية تتبع معادلة سرعة من الدرجة الثانية كما ان معاملات الديناميكا الحرارية بينت ان عملية الادمصاص كانت ذات طبيعة تلقائية وطاردة للحرارة.