Progress in Chemical and Biochemical Research 2020, 3(3), 251-268

Progress in Chemical and Biochemical Research

Journal homepage: www.pcbiochemres.com

Review Article

A review of Studies on the Removal of Methylene Blue Dye from Industrial Wastewater Using Activated Carbon Adsorbents Made from Almond Bark

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ARTICLE INFO

Article history

Submitted: 2020-02-30
Revised: 2020-05-11
Accepted: 2020-07-04
Available online: 2020-07-08
Manuscript ID: PCBR-2005-1099
DOI: 10.33945/SAMI/PCBR.2020.3.8

KEYWORDS

Almond Bark
Industrial Wastewater Containing
Methylene Blue Dye
Pollutants

ABSTRACT

The production of industrial wastewater containing synthetic dyes is one of the most important pollutants in the environment. In recent years, sustainable development and generational attention have led researchers to work on ways to reduce environmental degradation and reduce pollution spreads, but as industries become wider and larger, pollution from their activities, it threatens the environment more. Colors are an important class of pollutants that can be detected by the human eye. Although valuable water resources should be avoided, different technologies and processes are used to solve this problem. However, among the various methods available for dye removal, surface adsorption has taken a prominent place. Demand for efficient and low-cost methods of adsorption is growing and the importance of low-cost adsorbents for replacement of expensive adsorbents has increased. In this study, the method of chemical activation of almond shell was performed by phosphoric acid activating agent. It was found that the effect of phosphoric acid activating agent on almond shell increased adsorbent surface area and adsorption capacity. Studies have shown that the smaller the almond shell particle size, the higher the contact area of the activating agent and the resulting increase in absorption.

GRAPHICAL ABSTRACT

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Introduction

Adsorption (Activated Carbon): The use of charcoal in ancient times has been used for many applications. Hindu documents mention that carbon filters have been used for water treatment since 450 BC. Scratched wood, bones and coconut charcoal were used in the 18th and 19th centuries by the sugar industry for disinfectants. Activated carbon is a material that is designed to have a high degree of porosity and a wide surface area. During the purification of activated carbon, contaminants are attached to the surface of these carbon granules or trapped in small pores of activated carbon. This process is called absorption.

Activated carbon filters are efficient for the removal of some organic matter (such as odor, odor, and junk), chlorine, fluorine or radon from drinking water or wastewater. However, it is not effective for microbial contaminants, metals, nitrates and other inorganic contaminants. Activated carbon filtration is commonly used in concentrated plants and at the domestic level, for the production of drinking water and in industries for wastewater treatment. It is also a future therapeutic method for removing microbes both in the production of drinking water and in the treatment of pre-treated wastewater.

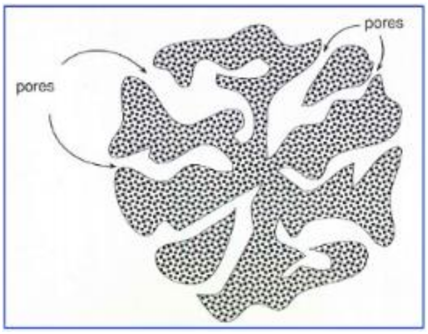

Figure 1. A typical carbon particle with multiple pores that provide a large area for water treatment [1].

Adsorption process: Adsorption refers to a process in which atoms or molecules accumulate in a gas or liquid solution on the surface of a solid or liquid material and form a molecular or atomic thin layer. Adsorbent is the material on which the adsorption process is carried out and the adsorbate is the material that sits on the surface of the adsorbent.

Common Steps of the Adsorption Process

In water treatment using adsorbents, molecules or ions are removed by adsorption from the liquid phase onto the solid phase. The efficacy of this method for removing various pollutants from contaminated water has been demonstrated. The adsorption process is performed in a single step or a combination of several steps including external penetration (contaminant penetration to the adsorbent outer surface), pore penetration (contaminant penetration into the adsorbent pores), surface penetration and adsorption onto the surface of the cavities.

The absorption process

The contaminant or dye as absorber penetrates the adsorbent due to the potential for diffusion. The extent of infiltration potential is determined by the concentration of adsorbed material and the area available on the outer surface of the adsorbent. The adsorbed material penetrates the absorbent cavities after penetrating the outer surface of the adsorbent. All available areas are occupied during the chemical or physical adsorption process. Observations show that Fick's second law applies to the adsorption process. According to this law, the rate of adsorption is inversely proportional to the square of the particle radius. As such, the adsorption process of smaller particles has a faster kinetics. This is not the case for all types of adsorbents. For example, although the fine zeolite particles have a high surface area, the adsorption rate of the adsorbed material on the adsorption regions in the larger crystals is higher than the adsorption rate on the smaller crystals, thus allowing faster penetration and thus higher surface adsorption.

The term adsorption is used to describe the fact that the concentration of adsorbed molecules at the solid contact surface is higher than that of the gas or solution phase. Adsorption on a solid surface is due to the attraction force of atoms or molecules on that solid surface. In practice, various forces, both physical and chemical, are effective in adsorption and the amount depends on the nature of the adsorbed material and the adsorbent, so that the material in a mixture can be separated, for example [1-2]. The diffusion of color pollutants into surface and groundwater has also caused major problems. The textile industry is responsible for releasing various dyes into the water's natural resources, which can be attributed to the lack of efficiency in dyeing techniques. More than 15% of dyes may enter the water directly when using reactive dyes [3]. In surface adsorption operations, a component is transferred from the gas or liquid phase to the solid surface. Applications of this process include refining sugar syrup and refining industrial or edible oils and removing pollutants from the air or other gas mixtures.

Colors; Types and Structure

Humans have been using colors for thousands of years. Scientists believe the first use of dyes and dyes dates back to 180,000 years ago. The first use of organic dyes dates back to about 4000 years ago. This information is based on the finding of blue in the Egyptian pyramids. Color molecules comprise two main parts: chromoforms responsible for the production of color and exochromes, which not only complement the chromoforms but also dissolve the dye in water and also absorb the color molecule into the fiber surfaces. Colors have many structural differences and are categorized in this way. This classification can be based on both chemical structure and color application. Another color classification is water solubility. Insoluble colors also include azoic, sulfur, dyeing and diffused colors. It can be sorted by type of major bonds as well as the chemical properties of the colors. [4]. Colored wastewater produced by various industries, including textile, paper, rubber and plastic, if discharged into the pre-treatment environment can cause significant environmental problems. For example, discharge of this type of effluent into the receiving water can cause toxicity to ecosystems as well as potential bioaccumulation of organisms in these environments. The concentration of paint in the wastewater varies depending on the type of industry involved. Wastewater, for example, in the leather dyeing industry varies between 1000 and 5000 mg/l. These dyes are usually chemically and photolytically stable and due to their complex aromatic structure, they remain unchanged during natural biodegradation processes and cause unpleasant odor and opacity. Methylene blue is one of the most common cationic dyes used in paper, hair, flax, wood and silk industries. Colors are aromatic organic compounds that absorb light at a wavelength of 350 to 700 nm (visible area). Depending on the chemical structure or chromophore, the colors are divided into 20-30 groups. Among the various colors, methylene blue is a multi-core aromatic compound that can not only cause respiratory problems such as shortness of breath and, if swallowed, cause burning, nausea, vomiting, diarrhea, and gastroenteritis.

Methylene blue application in industry

Methylene blue is a functional dyestuff that acts as a Red-X-indicator and has different colors (blue/colorless) in oxidized or reduced states. One of the milk quality tests to estimate the number of bacteria present in raw milk is the methylene blue revival test. Eosin methylene blue medium is used for germination of germs. Methylene blue is also used to stain tissues.

Light absorption properties of methylene blue dye

Absorption spectrum of methylene blue in terms of molar extinction coefficient: In this dataset, the maximum absorption rate of 1.7 (i.e. 98% of transmitted light absorbed) was observed at 665 nm passing 1 cm from the 10 μm methylene blue solution, the maximum absorption of light being about 670 nm. Adsorption properties depend on a variety of factors, including protein synthesis, absorption of other materials, and metachromacy - formation of higher order dimers and aggregates depending on the concentration and other interactions [5].

Water Purification: One of the priorities of today's human life is to have access to safe water. Millions of dollars are spent annually on the production of safe, germ-free drinking water. Groundwater in the US is so contaminated that scientists say every glass of city water a person drinks is a pharmacy, with each glass containing tens of ppm antidepressants and contraceptives. The quality of the water needed for self-consumption rarely corresponds to natural water. Drinking water is clear, cool, colorless, odorless and tasteless and free of pathogens and toxins. Such water is scarce in nature and if there are springs whose water is clean and pure it is not sufficient for human drinking and in addition, human beings directly and indirectly contaminate natural water.

The water used in any industry must also have specific specifications so that the equipment is not damaged and that the products produced are of the highest quality. Surface water needs more purification than groundwater.

Groundwater must be disinfected and in some cases more purified, such as reducing the hardness or removal of some solutes [6-8]. Surface or groundwater often contains impurities or undesirable properties. Basic water treatment processes such as coagulation, particle aggregation, settling, filtration and disinfection are carried out in the treatment plant.

There are methods, called preliminary purification, to reduce impurities or change the undesirable characteristics of water before reaching the treatment plant, thereby reducing the pressure on the main stages of water treatment.

Primary filtration is the physical, chemical or mechanical processes that occur prior to the main stages of water treatment, including recycling, preliminary chemical treatment, preliminary settling, and the use of fine-grained filters.

Table 1. Blue methylene absorption spectra in terms of molar extinction coefficient

Species	Absorption Peak	Extinction Coefficient (dm^3/mole·cm)
MB^+ (solution)	664	95000
MBH_2^+ (solution)	741	76000
$(MB^+)_2$ (solution)	605	132000
$(MB^+)_3$ (solution)	580	110000
MB^+ (adsorbed on clay)	673	116000
MBH_2^+ (adsorbed on clay)	763	86000
$(MB^+)_2$ (adsorbed on clay)	596	80000
$(MB^+)_3$ (adsorbed on clay)	570	114000

Physical absorption: Physical absorption is a reversible phenomenon due to the intermolecular attraction forces of the adsorbed material. The adsorbed material does not penetrate the crystal and the solid crystal lattice. In addition, it does not dissolve, but stays on the surface. In general, in equilibrium, the partial pressure of the adsorbed material is equal to the pressure of the gas phase contacted with it and by lowering the gas phase pressure or by increasing the temperature; the adsorbed gas is easily discharged and separated from the surface without deformation.

Chemical absorption: This type of adsorption is the result of solid chemical interactions with the adsorbed material. The adhesion forces are usually greater than those found in physical absorption. The heat released in the process of chemical adsorption is usually high and about a chemical reaction, for a material to be physically adsorbed and at high temperatures, chemical absorption may be observed. Chemical adsorption on catalysts is important.

The nature of adsorbents

Properties of adsorbents

The adsorbents must have their own-engineered properties, including the following:

1. There should not be too much pressure difference
2. They should not be taken out of bed with materials
3. Have good toughness
4. Keep it in the containers and remove it, so it can flow easily.

Definition of adsorbent

The solid that adsorbs on its surface is called adsorbent. The adsorbed material is called adsorbate. Adsorption occurs on the solid surface of the liquid solid [9]. Absorbent solids are usually consumed in the form of granules (spherical particles with a diameter of a few millimeters) and vary in size from 12 mm to 50 μm in diameter even the nanoscale will be captured and utilized by methods and technologies to be absorbed and utilized. Among these adsorbents can be bio-nano-polymers and nanostructured surfaces. For example, if they are used in a fixed bed with a gas or liquid flow, they should not cause too much pressure difference and should not be carried out by fluid flow. They must be good strength and hardness as not to be shattered by transport by their weight in the bed. If we want to move them in and out of storage containers, they have to flow easily. These are easily recognizable properties [10].

The adsorption property of solids is another issue. Absorption is a general phenomenon and all solids absorb some of the gases and vapors. However, for industrial purposes only some solids have the required absorption capacity. So solids that have a very specific adsorption property and are highly adsorbed, their chemical nature is related to the adsorption properties. However, just chemical identification is not enough to make it useful. For example, extraction, all pure butyl acetate samples that extract acetic acid from water have the same strength. This is not the case for the adsorption properties of silica gel to water vapor. These adsorption properties depend mostly on the method of fabrication, accessibility and the surface area of the adsorbent, adsorption, the history of adsorption and desorption on some materials. By itself, such adsorption can be attributed to the adsorption of diazo dye into bentonite [8]. In such processes, the heat of adsorption to the given environment and even the adsorbent itself increases, affecting the adsorption process. Many solids have the property of being able to absorb some of the gas or solute dissolved in the solvent.

Factors influencing the adsorption power of an adsorbent

Contact surface: One of the most important adsorption parameters is the contact surface of the two adsorbent and adsorbent species. As the contact surface increases, the amount of adsorption increases, the best adsorbents being substances that have smaller particles and, in other words, the higher contact surface area.

The most common adsorbents

1. Fuller's Earth
2. Activated clays
3. Bauxite
4. Alumina
5. Bone Char
6. Decoloring Carbons
7. Molecular Screening Activated Carbon. Molecular sieves should have 5 to 5.5 A° holes so that they do not cross paraffin hydrocarbons and do not cross isoparaffin hydrocarbons.
8. Synthetic Polymeric Adsorbents
9. Silicagel
10. Molecular Sieve
11. Silica

Can be mentioned. Each can be selected according to the type of material absorbed and the economic arrangements.

Concentration: The amount of adsorbed material per unit mass of adsorbent is a function of the solute concentration. It is usually reported in milligrams of adsorbed material per gram of adsorbent. Investigation of these two quantities at constant temperature yields an isotherm amount of adsorption. These isotherms have been studied by various people, among them the most important ones are the isotherms of Freundlich, the isotherms of Temkin, the isotherms of Langmuir, the isotherms of Dobnrad - Voskevich, the isotherms of Toos, the isotherms of Kisem, the isotherms Sipps, Isotherm BIT noted.

Temperature: In many cases, increasing temperature reduces the adsorption unless the adsorption is accompanied by a chemical reaction. In this case, the reaction temperature, according to Lushatelian principle, affects the total reaction as the whole system moves toward equilibrium. In other words, as the temperature increases for the adsorbents that are heated, the adsorption decreases and for the processes that are endothermic, the adsorption increases.

The type of material absorbed and absorbent

The adsorbed and adsorbent state coupled with their chemical reaction, their reversibility or their irreversibility also affect the adsorption.

Coals over: Such materials are high-capacity, low-cost adsorbents and are among the applications of this material in bleach. Today, charcoal is made in various forms:
Mixing plant materials with minerals such as calcium chloride, carbonization and mineral washing [9]. Mixing organic matter such as sawdust with porous materials such as volcanic rock, heating, and carbonizing until carbon deposits on the surface of the porous materials [11-13].
Carbonization of wood, sawdust and the like and activation by hot or steam air, lignite and bituminous coal are used as raw materials [14-15]. The use of acids to activate cheap adsorbents [16-18]. The use of ultrasonic to place adsorbent particles on the base. They are used for many purposes such as the decolonization of sugar solutions, industrial chemicals, drugs and liquids, water treatment, purification of animal and vegetable oils and in the recovery of gold and silver from cyanide solutions obtained from ore washing.

Activated carbon: It refers to a group of carbon materials with high oscillation and high internal surface which are unique because of their remarkable interior area, pore structure, high adsorption capacity, surface reactivity and low cost compared to inorganic adsorbents such as zeolite. Activated carbon is a high-capacity, low-cost adsorbent.

Activated carbon: Amorphous solid activated carbon has a structure with a high internal surface area that can absorb different molecules from the liquid or gas phase. It is made from a number of gross ingredients, including wood, coconut skin, and coal. Special processes for the production of activated carbons in powdered, granular and spherical forms have so far been developed. Activated carbon is obtained from pyrolysis of carbon or carbon-containing plant materials, such as wood, charcoal, kernels or fruit shells, such as coconut shells and is subsequently activated. Pyrolysis of carbon without the presence of air destroys the inorganic molecules from which a carbon powder material will be formed. The produced object has a high surface area and high porosity. Pyrolysis of carbon materials, without the presence of air, destroys inorganic molecules resulting from the heating of a product that eventually becomes a bitumen containing carbonated materials and becomes a carbon solid. The solid produced will have numerous holes and have a specific surface area of several square meters per gram. These values can range from 1500 m^2/gr to 2500 m^2/gr. In addition to wood, materials such as fruit kernels or synthetic polymers such as poly acrylonitrile or phenol are subjected to activation in subsequent phases. There are three main processes for activation carbon:

1. Steam activation
2. Activation with carbon dioxide
3. Chemical activation

Among the above three methods steam activation is the best environmentally and economically viable option.

While chemical activation results in the highest surface area and porosity. In the chemical activation process, the precursor is first prepared with a chemical active agent, which is often phosphoric acid and then heated to 450-700 ° C. The charcoal is then washed with water to remove the acid from the carbon and dry. The following figure shows a schematic diagram of the chemical activation process of wood. The shape of the pits is for the chemical activation method in a bottle.

Important parameters for activated carbon

1- Pore size
2. Particle Shape

Among the benefits of activated carbon are the following:

- High contact Level
- Pore-shaped Structure
- High absorption Capacity
- Ability to reactivate the surface
- Ability to use inorganic materials as catalysts
- The type of raw material used
- Carbonization conditions
- Type of actuator action
- Temperature
- Activation time

Types of adsorbents: The adsorbents used for dye removal can be classified into two types of adsorbents according to their origin.

Natural absorbents: The first species, which are natural sorbents, are mainly found in nature, such as those derived directly from living organisms, such as Artemia or plants. Usually, these types of absorbents come from the remains of their shells or body parts such as bones, hair and skin.

Synthetic adsorbents:

Synthetic adsorbents are called adsorbents in that the raw materials used are chemicals and do not come from living organisms.

Adsorption: In general, the movement of a component from one phase to the common phase of this phase with the second phase and accumulation of this component into the surface of the common phase is called the surface adsorption process [19]. In other words, the two-phase contact process is required. The first phase, which is partially separated and moves to the second phase, the fluid (liquid or gas) and the second phase, where the component or components accumulate on its surface can be either liquid or solid. If the adsorption process is carried out on the surface of a liquid, it is adsorbed on the liquid and if adsorbed on the surface of a solid, it is called the adsorption on the solid surface and is part of the fluid phase that adsorbs the solid to the adsorbed component and the solid. They are usually very porous called adsorbents. Movement of the component from the fluid phase and its accumulation and condensation on the surface of the adsorbent body will continue until the two phases are in equilibrium from a chemical potential point of view, although several factors including the adsorbent capacity are also effective in this phenomenon, however at this moment then the adsorption process stops.

The adsorbent surface is actually called the two-phase homogeneous layer. It can have variable depth. The depth of the adsorption layer depends on the type of adsorption and diffusion process of the adsorbed species and usually due to diffusion, the adsorbed compounds can penetrate from the depth of 5–5 nm to the adsorbent surface. Mass transfer to the adsorbent surface is an equilibrium process. Any type of adsorption process, both physical and chemical, reduces surface free energy. So it can be said that the absorption process is a spontaneous process that reduces the Gibbs free energy. According to the above, the adsorbed species are first adsorbed on the boundary layer and then penetrated to the depth of the adsorbent under the permeation process. Adsorption can be accomplished by many separations that are impossible or impractical by other separation techniques such as distillation, gas-liquid adsorption, and liquid-liquid extraction and membrane separation methods. It should be noted that due to its simplicity and wide application, distillation has a large share in traditional technology.

Since 1970, surface adsorption has been superior to the energy-dependent process of distillation, in some respects. Isolation by surface adsorption, however, is more economical when the separation coefficient 6 or selectivity 7 is much higher than the relative volatility coefficient. In other words, when the relative volatility is less than 1.25, as a relative rule, surface adsorption over distillation is preferred for separation. Therefore, the emergence of surface adsorption has increased the process and environmental applications of separation techniques. While many of these applications are only possible through the development of absorption technology. The adsorption process is often carried out in a fixed bed of adsorbent with periodic resuscitation operations on it. A conventional system consists of two parallel beds in which one is in absorption state and the other is in resuscitation. In large industrial units, the use of three platforms is common. As such, there are always two substrates being absorbed and one substrate being resuscitated.

Applications of adsorption process in water treatment industry

Activated carbon is a carbon adsorbent that dates back to 1600 BC. When activated carbon was used for medicinal purposes in Egypt, in Japan, at a depth of 120 meters underwater, a spring was found which was filtered using a charcoal ash filter and the source was related to the temple. Although the application of the adsorption process in water treatment is currently controlled by the production of flavor and organic matter, this process involves the removal of synthetic organic chemicals from color organic matter, disinfectant by-products and natural organic substances, as well as hazardous components such as paint and human health. Heavy metals have a great impact [20]. Just as any product has a defined standard and must adhere to it, drinking water also has physical and chemical standards and appearance as shown in **Table 2.** They are referred as appropriate water.

Background Research

The textile industry in any country can be considered one of its most important industries. Since the production of textile products is also possible in small industrial units, there is a large number and variety of manufacturers in the industry, which results in a large amount of waste and environmental pollution.

Synthetic dyes are widely used in the textile industry and there is a wide range of dyes used for dyeing various substrates and these compounds are widely used in various industries including textile, food, cosmetics and paper printing [21] and because of the xenobiotic nature they are generally resistant to degradation. About 15% of these dyes are released into the effluents in the dyeing processes. This dye from the textile industry wastes due to its structure causing serious environmental problems. Various colors and the use of large amounts of water in dyeing processes that is why dye removal has received considerable attention in industry or internal effluent in past few years. The biological, physical and chemical methods used for industrial textile wastewater treatment include microbial degradation, membrane purification, oxidation and ozonation.

Common treatment is often undesirable stagnation due to its high solubility and low degradability. The use of adsorption on solids is considered as the method of choice for the textile dyes removal. This economically efficient and economical method can lead to complete decomposition of wastewater.

Table 2. Physical and chemical properties of drinking water that standard organization has determined [20].

	Properties type	Desired value	Allowed value
Physical properties of drinking water	Colour	5 units	15 units
	Odor	2 units	3 units
	Opacity	5 units	25 units
	pH	7-8.5	6.5-9.2
	Composition	Maximum desired value mg/lit	Maximum allowed value mg/lit
Chemical properties of drinking water	Total hardiness	150	500
	Ammoniac	0.002	0.05
	Calcium	75	200
	Magnesium	50	150
	Iron	0.3	1
	Copper	0.5	1.5
	Sulphate	200	400
	Chloride	200	600

Commercial activated carbon is complex in the sense that it is designed for different types of applications. Adsorption on activated carbon is currently used due to its specific surface area and sufficient pore size to remove different types of dyes. Distribution most dye groups such as acidic, alkaline, reactive are found directly in the environment. These compounds are characterized by their high chemical toxicity, mutagenicity and carcinogenicity. Many studies have been done so far to develop effective and cheaper adsorbents in the field, such as the adsorbents of sugarcane, corn husks, rice bran, banana waste, coconut skin, sludge residue and carbon raw materials such as orange peel coal barley peel sawdust rice husk cereal straw castor seed husk prairie ash and pine cones. Comprehensive studies of the previous work literature indicate that in addition to being readily available, cheap adsorbents must exhibit high adsorption capacity. Previous work has discussed the optimal conditions of adsorption and the type of adsorbed material and the conditions of suitable environments for adsorption and the ability of the adsorbent to be activated carbon.

Research on the use of these two types of natural and synthetic sorbents has been discussed

Use of synthetic sorbents: Abnormal and synthetic adsorbents is a type of adsorbent that it is made from synthetic materials, such as synthesized polymeric materials or abnormal composites, from the beginning of the adsorbent and synthetic materials are their primary source. These adsorbents are often economically expensive and in some cases have attracted fans because of their selective absorption rate and selectivity.

Jeng Shi Woo *et al.,* have been able to remove methyl 2B violet from the aqueous medium by using cation exchange membranes. This membrane with a sulfonic acid group had a cross-section of 47 mm radius on a disk surface of 47 mm and a second membrane with phosphate groups was capable of exchange of 312 eq / disk with 47 mm dimensions. They were able to recover up to 60% adsorption by placing the adsorbent at 540 ° C for 1 hour. Shaobin Wang *et al.,* have investigated the reactivation of their zeolite adsorbents by physical and chemical methods. Jay Guijuan *et al.,* used chitosan and alumina bonds as a hybrid adsorbent for the absorption of copper (II) in their research.

Niyaz Mohammad Mahmoudi *et al.,* with the synthesis of PAC copolymer have evaluated its efficiency for dye removal. They have used Red 31, Red 80, and Acid Blue 25 for the model and obtained the elimination values of 3400 mg/g, 3448 mg/g and 3500 mg/g, respectively, for the 31, 80, and 25 color codes, respectively. Their results showed that PAC as a polymeric adsorbent exhibits high adsorption capacity.

Use of natural absorbents

Because of its abundance in nature and its good absorption and ease of upgrading, natural absorbents have attracted the attention of many experts. Many crops and animal waste such as leaves, seeds, nuts, fruits and bones and some animal components are readily and abundantly produced in nature and utilized because of their ability to be recycled and returned to the ecosystem. They have become much more convenient and useful as adsorbents and have attracted attention. Among the natural adsorbents used by the researchers the use of rice bran ash carbon from the Indian sourdough core and bran ash activated by bentonite and a vertebrate living organism, the use of raw pine wood and acid-treated wood or jojoba seeds can be noticed that have been evaluated by various researchers. There are typically more adsorbents for the removal of cationic dyes because they appear to have a high affinity for negative charge due to their positive charge on the nitrogen atom. For this reason, dyeing by these types of colors is easier in color-related categories such as textiles. In addition to the aforementioned adsorbents, there are also a number of adsorbents that describe some of the research that has been done to remove dyes.

Research on the removal of cationic and anionic dyes

Perz Gregory *et al.,* used bran ash to remove methylene blue dye and Vanquat *et al.,* to remove brillantiger dye. Sarah Davood *et al.,* have used raw pine as an adsorbent to remove Congo red and have provided the optimal process for it. To remove anionic dyes from aqueous media, some work has been done on the use of enhanced natural zeolite by Orwell Alvor and Aicha Matin. A mixture of aluminum hydroxide and magnesium hydroxide has also been used to remove reactive bright red dye by Yu Jiang Li *et al.,* There are two major ways to obtain activated carbon, including physical and chemical methods. A review of previous work shows that these two methods differ in the activation temperature stage and the additives added to the adsorbents in the pre-mixing phase. They are arranged to make comparison easier. To compare the adsorption power of the adsorbents, a parameter called Q_0 is used which indicates the maximum adsorption rate of the adsorbent monolayer. For example, researchers have done a number of different tasks, such as methylene blue dye, according to research done on brilliant color. The types of adsorbents used are shown along with the maximum capacity of each adsorbent. For better comparison, the absorbent has been drawn to the table. The adsorption power for the adsorbents obtained from the palm kernel fiber and the biomass obtained from the pine cone is the highest.

Based on past research to better compare and better evaluate the adsorption capacity of this type of adsorbent. Researchers have used many methods to convert raw materials into useful adsorbents with high porosity but the procedure and its general process. It can be seen that phosphoric acid and potassium salts have been used for chemical activation. According to the research done in the sources.

A review of research on pollutant removal, especially colors from aquatic environments

The discharge of industrial effluents containing various pollutants has caused environmental pollution and disruption of the ecosystem and environment of different animal species. In addition, through the seafood and agricultural products irrigated with effluents, the public health of human beings has been seriously threatened. Most recent research has shown a widespread increase in the removal of synthetic dyes from water and wastewater.

Table 3. Maximum methylene blue dye absorption by low-cost adsorbents and agricultural waste

Adsorbent	Single layer adsorption capacity (mg/g)
Leaves of pine trees	40
Biomass of pine cones	109.89
Beech sawdust (hornbeam) green (not dry)	9.87

Table 4. Maximum uptake of Bryantine dye by inexpensive adsorbents in nature and agricultural waste materials

Adsorbent	Single layer adsorption capacity (mg/g)
Rice husk ash (rice bran)	25.13
Ash Bagasse Ash	116.28
Indian rattan	52
Clay saklikent	9.7
Pre-treated sawdust	60
Polyacrylic acid hydrogel	17.54
Saccharomyces cerevisiae	65.3
Kaolin	65.42
Aspergillus marine venipuncture (carboxylic acid esterified)	384.6

Various methods have been used, such as adsorption on various types of adsorbents, chemical degradation by oxidation, photo degradation, and microbial application of activated sludge.

The advantages and disadvantages of each method are discussed in different sources. Extensive research has been carried out on the removal of dyes and heavy metals from various wastewaters, suggesting the application of surface adsorption knowledge and methods of absorbing and removing pollutants in this regard. Other types of dye adsorption methods include deposition methods, filtration technology, chemical processes, oxidation, electrochemical methods, advanced oxidation processes, biological processes and other methods.

The contaminant dyes investigated in various sources for removal include anionic, cationic and neutral dyes. Most of the work done on the removal of cationic dyes from different wastewaters has been discussed and presented by Paint *et al.*

A review of research on the removal of methylene blue from wastewater and aqueous solutions

Based on studies by Kamar *et al.,* 2010 in Seoul, Korea on the removal of methylene blue from aqueous solution with activated carbon from peanut shell as a new low-cost, methylene blue dye on bead shell adsorbent Peanuts were absorbed. A batch adsorption study was performed with variable adsorbent amount, initial dye concentration, contact time and pH. Studies have shown that the pH of aqueous solutions on dye removal due to removal efficiency increases with increasing solution pH. Experimental data were analyzed using Langmuir, Freundlich, Redlich-Peterson, Kub-Corigan, Mut, Temkin, Sips and Dobin-Raduskovic adsorption models using MATLAB 7.1. Experimental data corresponding to the following isotherms are obtained:

Redlich-Peterson> Toth> Sips> Koble-Corrigan> Langmuir> Temkin> Dubinin-Radushkevich> Freundlich

Based on its correlation coefficient values three simple kinetic models including a pseudo-first-order, pseudo-second-order relationship and in-particle diffusion equations were chosen to follow the adsorption process. It was shown that the absorption of aqueous methylene could be described by the pseudo-second-order equation.

The results suggest that activated carbon with peanut shell nut can be used as a low cost alternative to commercial activated carbon in removing paint from wastewater.

According to a study by Mohammad Harifu *et al.,* (Department of Chemistry, Dhaka University of Bangladesh) in 2012 regarding the removal of methylene blue with carbon made from Hass rice; possible use of activated carbon in rice husk as adsorbent to remove methylene blue from solution blue water has been studied. In this study, activated carbon, low cost rice husk using sulfuric acid and activated zinc chloride were used as adsorbents to remove aqueous methylene blue, a primary dye. The effects of various laboratory parameters, including adsorbent dose and particle size, initial dye concentration, pH and flow rate on the column process are investigated. Maximum aqueous methylene uptake by activated rice husk carbon at optimum conditions (dd) 140 μm partial measurements; flow rate: 1.4 mL / min; pH: 10.0; initial methylene blue (0.4 mg/l, etc.) was observed up to 97.15%. The results suggest that activated carbon of the rice husk can be used as a low cost alternative to commercial activated carbon in waste treatment plants to eliminate essential dyes. This low-cost and effective removal method can be a promising solution for removing the crystalline purple from the effluent.

Experimental studies were carried out by Mousavi *et al.,* in 2012 to remove methylene blue dye from synthetic wastewater using pistachio peel as an adsorbent. Materials and Methods: The adsorbent was prepared from pistachio green husk and after collection and drying, it was powdered and kept away from moisture. The samples required in this experiment were synthetically prepared in the laboratory using methylene blue dye. In this experiment, the effects of initial soluble pH variables, adsorbent dose, methylene blue dye concentration and the effect of contact time of entry were investigated. The mixture was equipped with an incubator equipped with a mixer. Methylene blue dye concentration was measured using UV/Visible spectrophotometer at 665nm. Data were analyzed by using Excel software. The results showed that with 70 min contact time and adsorbent dosage of 1.5 g/L at optimum pH 8, removal efficiency increased from 6.94 to 7.99% by decreasing methylene blue dye concentration from 400 to 100 mg /L. Conclusion: Using pistachio peel as a low-cost adsorbent can remove methylene blue dye from aqueous solutions with high efficiency.

Safdari *et al.,* (2013) conducted their research on removing reactive blue dye 19 from synthetic textile wastewater by olive ash sorbent. The aim of the present study was to investigate the efficiency of olive kernel ash in removing reactive blue dye 19 from synthetic textile wastewater and the effect of different parameters on the adsorption process. Materials and Methods: Influence of parameters such as adsorbent mass (0.05 to 1.5 g /100 mL), contact time (10 to 180 minutes 24 hours) and 4 to 10 pH at initial concentrations of 10 and 50 mg/l the removal of the desired color was investigated. Residual dye concentration was measured by UV-VIS spectrophotometer. Finally, after determining the optimum conditions, Langmuir and Freundlich adsorption isotherm models were analyzed. According to the results of the present study, increasing the adsorbent mass and contact time resulted in an increase in removal efficiency and an increase in pH and concentration. Initial dyeing resulted in reduced removal efficiency. The removal efficiencies at concentrations of 10 and 50 mg / L of RB19 dye decreased from 100% to 87% and from 95.4% to 66% with increasing pH from 4 to 10, respectively. The results showed that the reactive blue 19 absorption by the olive core ash reached equilibrium in 180 min. This study showed that reactive blue 19 adsorption using olive kernel ash was in better agreement with the Langmuir model (R2=0.966). Environmental pollutants should be used.

Experiments were carried out by Delor Shah Vali *et al.,* in 2015 to remove methylene blue dye using Conocarpus erectus plant adsorbent by using Batch technique to separate methylene blue from aqueous solutions. Methylene blue is widely used in many industries. Due to environmental protection regulations, it is important to remove this dye from industrial wastewater. In this study, a large and inexpensive adsorbent of Conocarpus erectus was used.

In order to obtain optimal adsorption conditions, the influence of important variables on the efficiency of adsorption process such as pH, initial dye concentration, adsorbent dose, contact time, adsorbent particle size, stirring speed and electrolyte effect were investigated. The optimum conditions for maximum dye removal were pH = 5.7, with absorbent particle size of 77 mesh, contact time of 55 min, adsorbent dose of 0.5 g, initial color concentration of 577 mgL^{-1} and solid period of 315 rpm. The removal efficiency of this dye was obtained from the adsorbent under optimum conditions to a concentration of 777 mgL^{-1} with 95% removal rate. The effect of electrolyte was investigated and the results did not show a significant effect on the color removal percentage change. In addition, Langmuir and Freundlich adsorption isotherm models were studied and found to be in good agreement with Langmuir model. The absorbent capacity was 621 mgg^{-1}. Thermodynamic values such as Gibbs free energy change (ΔG), entropy S and enthalpy (ΔH) were calculated at temperatures of 301, 316 and 331 °C with accuracy of ± 2 °C. The negative ΔG value indicates that the methylene blue adsorption process to the adsorbent on Conocarpus erectus is spontaneous and the negative ΔH value indicates exothermic adsorption process. Kinetic studies were also performed and it was found that the pseudo-quadratic kinetic model fits better to this system. The research results of Darwishi Cheshmeh Soltani *et al.,* on the efficacy of activated carbon produced from sapwood in removing methylene blue from aqueous solution showed that the preparation of activated carbon from sapwood has high potential for removal of dye molecules. The values of dye adsorption capacity at pH 3, 7 and 11 for the initial dye concentration of 50 mg/l and the adsorbent mass of 0.1 g/0.1 l for 30 minutes were 38.66, 40 and 48.5 mg/g, respectively. Concentrations of 50, 100 and 150 mg /l at 7 pH adsorbent mass 0.1 g / 0.1 and 30 min time were 40, 69.66 and 78.04 mg/g, respectively. The adsorption data follow the Langmuir adsorption isotherm model (R_2 = 0.99). Based on the results of this study, activated carbon prepared from Astragalus can be considered as an efficient adsorbent for dye removal from aqueous phase.

Najafpour *et al.,* have investigated the effect of nuclear and bitter olive fruit adsorbents on synthetic wastewater removal from synthetic wastewater in 1395. The purpose of this study was to determine the efficiency of kernel and bitter olive fruit adsorbents in removing methylene blue dye from synthetic wastewater. In this study, Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM) were used to determine the structural properties of the adsorbent. The effect of various parameters such as initial dye concentration (100-100 mg/l), adsorbent amount (0.1-1.1 g/l), contact time (0-60 min) and pH (4-10) on the dye removal rate studied. The kinetics and adsorption isotherms of dye were also investigated.

The dye concentration was determined by UV/ Vis spectrophotometer at 665 nm. The maximum dye removal was obtained at 32.5 mg/l, 0.85 g/l absorbent dose, 45 min contact time, and pH 8.5 at 85%. Initial dye concentration had the highest effect on removal rate (p = 0.0001). The results showed that the kinetics of the adsorption process were quasi-quadratic kinetic model (R_2 = 0.99-0.95) and the equilibrium data of Langmuir isotherm model (R_2 = 0.9). The results showed that bitter olive kernel and fruit had the ability to remove methylene blue dye. The optimum pH for removal of this dye by the adsorbent is alkaline and most textile wastes have an alkaline pH.

In Saudi Arabia, in 2017, study by Amin *et al.,* the effective absorption of methylene blue dye using activated carbon was derived from rosemary, inactivation efficiency of inactive rosemary (RM) and activated carbon derived (RMAC) was studied to remove methylene blue (MB) dye. RM and RMAC showed maximum adsorption capacity of 153.17 and 110.67 mg G^{-1}, respectively, for optimal batch conditions. MB absorption data of both RM and RMAC are better described by the Langmuir isotherm model than Freundlich isotherm models. However, the former showed a physical absorption rate with an average free energy of 8.08 kJ mol^{-1} and the latter showed a chemical reflectance with an average free energy of 28.87 kJ mol^{-1}. The MB adsorption of both adsorbents follows the pseudo-second-order kinetic model. The MB dye adsorption process was found to be a spontaneous and external reaction for the RM adsorbent, while the RMAC reflects the spontaneous and intrinsic nature of the MB adsorption. This study showed that RMAC can be used as an effective adsorbent for removing MB dyes compared to its inactive form.

Sharifi *et al.,* (1997) carried out a comparative study on the amount of methylene blue dye removal using activated carbon prepared from plant species of Sabzevar desert region. It was prepared from plant species of Sabzevar desert. The present study was a laboratory-scale experimental study. All methylene blue adsorption experiments on activated carbons produced from *Zygophyllum eurypterum* and *Calligonum comosum* plants in batch reactor were investigated in 100 ml volumes containing 50 ml of specific concentrations of methylene blue and adsorbent at different contact time pH and temperature. The results of the experiments showed that the removal efficiency of methylene blue by activated carbon produced from the *Z. eurypterum* plant was higher than that of *C. comosum*. The best removal efficiency of methylene blue was at pH =7, adsorbent concentration 0.04 g/l, contact time of 10 min. The isotherm studies in both carbon types of the Langmuir model and the adsorption kinetics were of the quadratic type. In general, the results of this study indicate that activated carbons from two types of *C. comosum* and *Z. eurypterum* are somehow native to the region. Given the acceptable efficiencies above 90% and their low cost, they can be suitable options for the treatment of wastewater containing paint.

According to studies by Hee Jeong Choi *et al.,* (Department of Health and Environment, Catholic University of Quandong) on the wireless uptake of aqueous methylene from aqueous solution using an agricultural bioadsorbent separator core in Korea in 2018, the most common blue methylene blue (MB) dyes were removed by using abandoned product by-products. This experiment is very important because it is a recycling of resources and the use of environmentally friendly adsorbents. According to Hauser ratio and porosity analysis, corncob has a good flow ability in many absorbent and pores materials which is very useful for absorbing MB. As a result of the experiment, MB concentrations of less than 0.005 g/L with 10 g/L corncob bioadsorbent were removed and the maximum citrus uptake capacity for MB dyes was obtained at 417.1 mg/g. In addition, the MB uptake process on the corncob was a physical process with respect to the uptake energy analysis. Corncob can efficiently and environmentally remove MB in aqueous solution and is highly cost-effective and can reclaim abandoned resources.

According to research conducted by Francisco Silva et al. In Brazil in 2019, the colorless uptake of methylene blue was achieved using natural bioadsorbents made from weeds, which aim to use vegetables, although in nature, it is great but there are few uses for it. The weeds used here, Cyanthilium cinereum (L.) H. Rob (CCLHR) and Paspalum maritimum (PMT) found in the Amazon region of Belém in Para Brazil help remove water methylene pollution problems. Using other materials for economic viability and processing is used through the process of dye absorption. The influence of parameters such as bioadsorbents dose, contact time and initial dye concentration were investigated.

Characterization was accomplished using SEM to confirm material morphology and spectroscopy in the FTIR region. In the case of adsorption mechanism, the physical adsorption mechanism was predominant. The time it took for the system to reach equilibrium for both adsorbents was 50 min followed by a kinetics described by the pseudo-second-order model. The adsorption isotherm data for the PMT are better absorbed by the Langmuir model and the adsorption capacity (Unknown node type: span Unknown node type: span Unknown node type: span was (569/176 mg/g). The CCLHR was better tuned with the Freundlich model and had a maximum adsorption capacity of 76.3359 mg/g. Therefore, such weeds are promising to absorb methylene blue in the effluents.

Conclusion

Whereas this research was initially aimed at developing a new method and creating innovation in research; therefore, this study is a novel method for industrial wastewater treatment based on the performance of methylene blue dye removal from industrial wastewater and the use of raw material as adsorbent as well as the type of data analysis and parameter analysis. In general, the main difference between the method used in this research and the previous research is in three cases:

1. Since the previous research has been done to remove methylene blue dye from aqueous solutions, but in this research, methylene blue dye has been removed from industrial wastewater especially textile and dyeing industries.
2. In previous studies, methylene blue dye removal from aqueous solutions was performed by using peanut powder adsorbent whereas in this study, the adsorbent is made of almond peel, the surface area and absorbability and the adsorption and surface properties of almond and peanut shell are different while almond are much stronger in texture and shell structure and more durable than peanut shell. As a result, almond shell requires much higher and higher temperatures than peanuts when carbon is made and strength and durability are comparable to walnut shell.
3. Considering that in previous researches methylene blue dye removal from aqueous solutions, data analysis and performance parameters of exploitation parameters were determined by determination of adsorption, equilibrium isotherms, drawing tables and graphs by Excel software. But in this study, data analysis and charting was performed by RSM software for the first time in the process of methylene blue dye removal from industrial wastewater using carbon made from peanut shell then optimum test conditions were evaluated according to the desired operating parameters. Accordingly, this research is considered as a new technology and method in the process of industrial wastewater treatment by carbon adsorbents made from almond shell.

Acknowledgements

Financial support by Ahvaz Branch, Islamic Azad University is gratefully acknowledged

Conflict of interest

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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HOW TO CITE THIS ARTICLE

R. Rahimian, S.,Zarinabadi, A review of studies on the removal of methylene blue dye from industrial wastewater using activated carbon adsorbents made from almond bark, Prog. Chem*. Biochem. Res*. 2020, 3(3), 251-268

DOI: 10.33945/SAMI/PCBR.2020.3.8

URL: http://www.pcbiochemres.com/article_110103.html