Acta Universitatis Sapientiae
Agriculture and Environment, **14** (2022) 29–44

DOI: 10.2478/ausae-2022-0003

Methylene blue and Congo red removal by activated carbons: A current literature

Yeo Shi HAO,[1,2] Norasikin OTHMAN,[1,2]
Muhammad Abbas Ahmad ZAINI[1,2]*

[1] Centre of Lipids Engineering & Applied Research (CLEAR), Ibnu-Sina Institute for Scientific and Industrial Research (ISI-SIR), Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

[2] Department of Chemical Engineering, Faculty of Chemical & Energy Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia
e-mail: yeoshihao95@gmail.com, r-nora@utm.my, abbas@cheme.utm.my

*Corresponding author

Manuscript received 23 June 2022; revised 18 July 2022

Abstract: Dye is a major source of water pollution. This mini-review highlights the origin of dye, its removal strategies, and the recent literature of methylene blue and Congo red adsorption by activated carbons. Adsorption is a unique process that relies upon the physicochemical properties of the activated carbon and the inherent characteristics of dye. Also, factors affecting adsorption, such as contact time, temperature, and concentration, were discussed to gain insight into dye removal mechanisms.

Keywords: activated carbon, adsorption, dye, methylene blue, Congo red, wastewater treatment

1. Introduction

Dyes are a common organic contaminant in many areas across the world. A British scientist named William Henry Perkin discovered the world's first synthetic purple dye in 1856. It was originally known as Tyrian purple, but after being commercialized in 1859, it was renamed mauve or aniline purple [1]. Dyes are commonly used in the textile and food industries for the purpose of colouring products. Many commercial dyes are manufactured each year, resulting in approximately seventy thousand tonnes of dye pollution. Dyes in water are less biodegradable due to their chemically stable aromatic molecular structures [2].

Due to the excessive discharge of dyes into environment, the textile industry is one of the major contributors to dye pollution. The amount of waste dye in the textile industry is 3,000 ADMI, which exceeds the department of environment's allowable limit of standard A (100 ADMI) and standard B (200 ADMI) in Malaysia [3]. Dye wastewater is discharged into a river or waterway, contaminating the aquatic environment [4]. Dyes have certain adverse effects on the environment and humans. For example, dyes have a significant effect on bacteria, and hence affect their growth. Dyes, considered carcinogenic, can also cause serious diseases in humans. Also, dyes can affect the aquatic living organism by causing chemical and biological activities in rivers, as well as consuming oxygen that is dissolved in the water [5].

Dyes are coloured, ionizing, and aromatic organic substances that have a specific affinity for the substrate to which they are applied in an aqueous solution. It colourizes a substrate inasmuch as the colouring remains resistant to washing, heat, light, and other conditions. However, not all dyes are coloured substances, as there are whiteners or optical brighteners that are also referred to as “dye”. Because they contain carbon, most dyes are organic. In the visible area, dyes strongly adsorb light, and the physical and chemical interaction between the functional groups of the dyes and those on the support allows a strong bond between the dye and the support. In other words, physical forces, such as hydrogen bonding (van der Waals), and ionic forces enable dyes to be physically linked to the fibre, and in certain situations dyes are chemically bound to the substrate via covalent links [6].

2. Classification of dyes

Dyes can be grouped in several ways at the international level to ensure an easier import and export trading and dye manufacturing. Different dyes can be classified based on their chemical composition, application, colour, dyeing support, and commercial name. Chemical composition and application are the most used classification criteria. In the dyeing industry, dyes are classified mostly based on application rather than on chemical composition. The chemical composition of a dye indicates how many chromophores it has, but it does not reveal the dye's structural characteristics [7]. *Table 1* summarizes the classification and application of dyes.

Concerning the dyes' class, colour, and overall composition as found in the Colour Index of the Society of Dyers and Colourists, they are basically separated into three broad categories, which are as follows: dyes containing anionic groups, dyes containing cationic groups, and special colourant class. Numerous compounds from various dye classes, such as acid, direct, and reactive dyes, contain carboxylic acid or sodium salts of sulfonic acid groups [8]. Although these anionic dyes have different structural characteristics and substrate affinity, they all have the same property of providing water solubility and ionization to the dyestuff.

Table 1. Classification and application of dyes [7]

Dyes	Application
Acid dyes	Coloured anions applied to silk and nylon at low pH.
Basic dyes	Coloured cations used on polyacrylonitrile textiles with acid side-chains; mainly used on proteinaceous fibres and tannic acid-treated cotton.
Natural dyes	Dyes made or extracted from plants or animals.
Direct dyes	Acid dyes with big molecules that can directly bond to cellulose fibres.
Disperse dyes	Insoluble coloured substances in fine suspension which infiltrate hydrophobic materials.
Reactive dyes	Coloured substances that have side-chains which react with the substrate to form covalent bonds; used to dye cellulose and other materials.
Azoic dyes	An insoluble azo dye formed within the substrate through the reaction of diazonium salt with naphtol.
Solvent dyes	Coloured substances that are only soluble in hydrophobic solvents and used to colour liquids and polymers.

Basic dyes are also known as cationic dyes, and these coloured cationic salts belong to the family of amine derivatives. The basic groups in the structure of basic dyes enable the migration and the reaction of basic dye cations with the acidic or negatively charged fibre surface, resulting in an ionic linkage formation. These cationic dyes contain amine side-chains, which are protonated in acidic solutions, or quaternary nitrogen atoms, which are cationic in neutral or high pH environments. A non-conjugated chain of carbon atoms may be bound to the charged group [9]. Basic dyes have the advantage of producing bright colours and intensities, as well as being extremely quick on acrylic fibres. These cationic dyes have a high tinctorial value and are soluble in mild acidic conditions. Basic dyeable acrylic, cationic dyeable polyester, wool, silk, and nylon are among the fabrics to which basic dyes are applied. Basic dyes have also been found to be extremely strong and effective colorants for ready-made textiles such as acrylic fibres [10].

An example of a special colourant class is disperse dyes. The small polar dye molecules used in the dyeing of hydrophobic synthetic fibres, such as nylon, acetate, triacetate, polyester, and other manufactured fibres, are known as disperse dyes. Disperse dyes, unlike other cationic or anionic colourants, contain anthraquinone or azo groups but do not contain either positively or negatively charged groups. Disperse dyes have good light and wash fastness, as well as provide powerful bright colours although have a low water solubility [11].

2.1 Methylene Blue

Heinrich Caro, a German scientist, synthesised methylene blue dye in 1876 by oxidizing dimethyl-4-phenylenediamine in the presence of sodium thiosulphate [12]. Methylene blue is also known as methylthionine chloride, having the chemical formula of $C_{16}H_{18}ClN_3S$. Some of its characteristics are: it is a dark green powder, has a deep blue colour when diluted in water, and is odourless. In addition, it has distinct physicochemical characteristics that are dependent on the polar co-solvent in solution. Methylene blue, like most organic dyes, does not obey Beer's Law, which is related to the light absorption properties of the substance through which light passes. This is linked to the reversible formation of dye aggregates, which is one of the characteristics of organic dyes [13].

The medical sector and the textile industry are the two main applications of methylene blue. In the medical sector, Paul Ehrlich was the first to employ this dye to treat malaria in 1891 [14]. Even though its mechanism in antimalarial activity is undetermined, its use in the treatment of malaria has proven to be quite effective [15]. It is also widely used to treat methemoglobinemia, Alzheimer's disease, and as a tracer in the mapping of sentinel lymph nodes during gynaecologic laparoscopy [16].

Next, methylene blue is widely used in the textile industry for colouring products, as well as in the cosmetic, pharmaceutical, and paper industries. It is a cationic dye that is widely used in the textile industry to dye wools, cotton, and silk, as well as for hair colouring and paper coating. The increasing use of dyes in the industries results in wastewater containing excessive amounts of dye, which is then discharged into the environment. Textile industrial wastewater is one of the most environmentally hazardous wastewaters [17]. Therefore, more studies should be focused on its removal from wastewater to avoid the harmful effect on the health of living creatures.

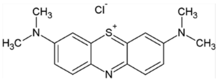
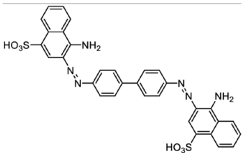
2.2 Congo red

Congo red was reportedly created in 1884 by Paul Bottiger, a German scientist who was looking for a pH indicator [18]. It is a synthetic compound with a variety of formal chemical names, but each molecule is made up of two molecules of naphthionic acid (1-naphthylamine-4-sulfonic acid or 4-aminonaphthalene-1-sulfonic acid) linked by azo groups to one molecule of benzidine (diaminophenyl or 4-(4-aminophenyl) aniline). Horobin and Kiernan (2002) gave Congo red the Colour Index number 22120 and the name Direct Red 28. The molecular formula is $C_{32}H_{22}N_6Na_2O_6S_2$. At a pH range below 3, it appears as a blue-violet colour, while it changes into red colour when the pH is above 5, and it is also odourless [19]. Due to its high solubility in water, Congo red can be easily removed via adsorption using carbonaceous adsorbent or activated carbon.

Congo red is mostly used in two main sectors, the medical and the textile. Its main application in the medical sector is in the diagnosis of amyloid. Bennhold described the staining of amyloid with Congo red in a short technical paper published in 1922, and this is now one of its most common applications. Bennhold was not, however, the first to use this dye as a microscopy staining. In 1886, Griesbach investigated numerous azo dyes, but he did not mention amyloid. Bennhold is credited with being the first to report its use in amyloid detection. This was identified in a study of Congo red intravenous injections, which had previously been used to measure blood volume [20].

Congo red is widely used in a variety of industries, including textile, printing, leather, paper, pulp, and cosmetics, and a large amount of its effluent is released into the aquatic system, particularly during dyeing processes. As a result, the overuse of the dye pollutes the environment and has become a major challenge for environmental protection organizations. Benzene and naphthalene rings in Congo red cannot be degraded using traditional methods. Due to the presence of an aromatic structure, it has a high optical and physiochemical stability [21]. Therefore, more studies should be focused on the removal of methylene blue and Congo red from wastewater. *Table 2* summarizes the characteristics of these two dyes.

Table 2. Characteristics of methylene blue and Congo red

Dyes	**IUPAC name**	**Commercial name**	**λ_{max} (nm)**	**Molecular structure**	**Reference**
Methylene Blue	[7-(dimethylamino)-phenothiazin-3-ylidene] dimethylazanium chloride	– Basic blue 9 – Methylthioninium chloride – Solvent Blue 8 – Swiss blue	650		[22]
Congo Red	disodium-4-amino-3-[4-[4-(1-amino-4-sulfonato-naphthalen-2-yl)-diazenylphenyl]-phenyl]-diazenyl-naphthalene-1-sulfonate	– Direct Red 28 – Direct Red K – Haemonorm – Solucongo	497		[23]

3. Dye removal technologies – An overview

Dyes are difficult to remove from wastewater because of their high toxicity and tinctorial value, which makes them visible even at low concentrations. Despite this, a variety of wastewater decolourization techniques have been developed, which can be classified into three categories: physical or physicochemical techniques, chemical techniques, and biological techniques [24]. Each dye removal technology has different applications, advantages, and drawbacks. In the following section, these dye removal techniques are further discussed.

3.1 Physical and physicochemical treatment

Dyes are physically removed from the wastewater in the course of the physical or physicochemical treatment. Physical, chemical, or biological unit processes are used in physicochemical wastewater treatment; in most cases, the physical process is in the first stage, followed by a sequence of single-unit processes. This means that the physical treatment removes dyes using specific equipment, without the use of any chemicals or reactions, whereas physicochemical techniques combine physical and chemical processes with the use of substances, such as coagulant and flocculant, to improve dye removal efficiency. Physical dye removal techniques include adsorption, ion exchange, and membrane filtration, which includes reverse osmosis, nanofiltration, microfiltration, and ultrafiltration, while physicochemical treatments include precipitation, coagulation, and flocculation [25].

Coagulation and flocculation are two physicochemical techniques that have been used in industrial wastewater treatment and decolourization over the years. Since it removes colloidal particles of turbidity, colour, and bacteria, this traditional method belongs to the initial treatment in an overall wastewater treatment scheme. The coagulation process does not remove all types of dyes [26]. Cationic dyes, for example, do not coagulate at all, whereas acid, direct, and reactive dyes coagulate in most cases, but their flocs are of poor quality and cannot settle without the addition of flocculant. Only disperse dyes coagulate well and sink rapidly.

Membrane filtration is a physical treatment that removes the dyes from industrial effluent in a continuous process. The micropores and selective permeability of the membrane are used to filter and separate residual dyes and pollutants from the treated water. In membrane separation processes, such as microfiltration, ultrafiltration, nanofiltration, and reverse osmosis, the membrane pressure is also a critical factor. This technique is highly effective, simple to adopt, and resistant to temperature and microbial attack, but its drawbacks are membrane fouling and clogging, as well as a high cost [27].

Adsorption is one of the most effective methods for eliminating dyes and other stable pollutants among all treatment methods. Furthermore, this physical treatment is cost-effective, simple to operate, and produces a high-quality product. In the absence of any reaction, the adsorption process involves the spontaneous accumulation of molecules of a gas, liquid, or vapour at the contacting surface. Physicochemical parameters, such as adsorbent surface area, dye adsorbent interaction, particle size, pH, temperature, and contact time, influence adsorption [28]. Adsorption efficiency is also influenced by the properties of the wastewater and the type of carbon used. Activated carbon, peat, coal, wood chips, silica gel, and other materials can be used for adsorption.

Ion exchange technique, on the other hand, cannot accommodate a wide range of dyes, and thus it is rarely used in the decolourization of dye effluent. In this physical treatment method, dye effluent passes through ion exchange resins to allow anions or cations to exchange until the exchange sites are saturated. To avoid adsorbent loss, the spent adsorbent can be regenerated. Nonetheless, because organic solvents are expensive and dispersed dyes are resistant to ion exchange, it is a high-cost treatment [29].

3.2 Chemical treatment

Chemical treatment employs a variety of techniques to remove dyes from textile wastewater, including ozonolysis, chemical oxidation, and reduction. When the specific chromophore of colour is decreased and the dye molecules are broken down into small fragments, decolourization by chemical techniques occurs. Chemical treatment methods such as oxidative treatments are commonly used in industries due to their ease of use. Despite this, most dyes are stable, and mild oxidation conditions are insufficient to remove dyes from wastewater. To improve dye removal in oxidative treatments, strong oxidizing agents, such as chlorine, ozone, Fenton's reagent, sodium hypochlorite, or other oxidizing alternatives, are used [30].

Chlorine is a good dye-oxidizing agent, and recent research has shown that it can be used for dye removal. Chlorine gas or sodium hypochlorite (NaOCl) can be used in the chlorination process. Chlorination can rapidly remove acid and reactive dyes, while direct and disperse dyes are resistant to chlorine treatment, even at high chlorine concentrations. Although chlorination is an effective and low-cost method of removing dyes, it can react with nitrogen-containing components, resulting in the formation of undesirable compounds [3]. The public has expressed a strong opposition to chlorination because it produces harmful chlorinated chemicals.

Using Fenton's reagent as an oxidant is another chemical oxidative technique. The Fenton reaction is widely used in the preliminary or primary treatment phase to manage sewage that is resistant to biological treatment and dangerous to all living beings. The hydroxyl radical is a powerful oxidizing agent that completely converts organic materials, including dyes, to water, carbon dioxide, and inorganic substances. Although this technique has a high efficiency in dye and COD removal, it still has several significant drawbacks, including the large amount of sludge produced, pH manipulation, which necessitates a significant amount of acid and alkali, the need to reduce excess iron concentration, and unfitness for final effluent emission [31].

Due to the characteristic of high instability, ozone is a stronger oxidizing agent than chlorine. Oxidation with ozone can break down detergents, chlorinated hydrocarbons, insecticides, aromatic substances, and phenols. Ozone oxidation is only effective for specific types of dyes: for example, a significant percentage of reactive dyes can be removed via ozonation, whereas the removal of azoic and basic dyes in wastewater is only moderately effective. Despite this, ozonation fails to separate dispersed dyes from the textile effluent. In other words, ozonation works best with molecules that are double-bonded [32].

Irradiation, in addition to oxidative methods, is a conventional chemical treatment that uses electron beams or gamma rays to destroy organic contaminants and harmful microorganisms in wastewater. When there is enough dissolved oxygen present, radiation can efficiently rupture organic pollutants. Due to the extremely rapid exhaustion of dissolved oxygen, a consistent and sufficient resource is required, which has an impact on operating costs. Although irradiation is a simple and effective technique, its use on a broad scale is limited due to maintenance and cost considerations [33].

3.3 Biological treatment

Dyes are removed from wastewater via adsorption on activated sludge or the biological digestion of dye molecules in biological treatment. However, because dye components are not a source of food for microorganisms, the competence of biological agents in the dye removal of dye wastewater is ambiguous and inconsistent. Bacterial breakdown of organic substances can take place in either aerobic or anaerobic environments. In other words, based on the oxygen requirement, biological treatment methods can be divided into aerobic and anaerobic treatment [34]. Nonetheless, dissolved oxygen concentrations in water may decrease because of rapid development with increased water pollution.

4. Adsorption of dyes

Heinrich Gustav Johannes Kayser, a German scientist, coined the term “adsorption” in 1881. Adsorption varies from absorption in that the former is the attraction between a substance and the outer surface of a medium termed adsorbent, whereas the latter is when a substance diffuses into a medium to produce a solution [35]. Because of capillary pressure, absorption is the fundamental driving force for transferring bulk fluid into a substance. Adsorption occurs when the atoms, ions, or molecules of the adsorbate bind to the surface of the adsorbent.

Adsorption is described as the spontaneous accumulation of gas, vapour, or liquid molecules at the contacting surface without any reaction. Adsorption is a phase of equilibrium in which the adsorbent meets the bulk stage and the interfacial layer, and it can occur in a variety of systems, including liquid–gas, liquid–liquid, solid–liquid, and solid–gas. In the evolution of industrial-scale adsorption processes, solid–liquid and solid–gas interfaces are equally the most common ones. Adsorption is defined as the penetration of the adsorbate molecules into the mass solid stage, whereas adsorbate is defined as the material in the adsorbed state [36].

Many researchers are interested in the development over several years of novel categories of solid adsorbents such as activated carbon fibres, carbon molecular sieves, microporous glasses, and nanoporous substances. Some adsorbents are used extensively as catalyst supports, catalysts, or desiccants, while others are used for liquid purification, gas separation or storage, pollution management, and respiratory protection. They are also interested in converting easily accessible and low-cost biomass into adsorbents, such as banana stems, mangosteen peels, oil palm, tea waste, and palm shell [37]. In terms of industry, industrial adsorbents can be divided into two categories: carbon adsorbents and mineral adsorbents.

4.1 Adsorption phenomena

There are multiple applications linked to the adsorption mechanism, including gas phase, liquid phase, and environmental applications. Gas phase applications include moisture removal in gases and fluids with activated alumina and nitrogen generation from air with carbon molecular sieves, while liquid phase applications include water treatment and protein uptake at the solid–liquid interface. Adsorption heat pumps and adsorption gadgets in spacecraft environmental control are examples of environmental applications. The adsorption process is used on a large scale in the industry for many applications: for instance, the separation and purification of gas and liquid blends, air, isomers, and bulk chemicals, water treatment, dehumidification of liquids and gases, chemical recovery from industrial gases, and removal of impurities in liquid and gas media [9].

Certain adsorbates in gas and liquid mixture are applicable in adsorption-related applications. The pore size and arrangement of solid adsorbents should be large enough to ensure rapid diffusion for adsorption-related operations. Generally, the van der Waals forces between the adsorbate and the adsorbent have a significant impact on selective adsorption [38]. Often, the higher the BET area (or pore volume), the greater the removal capacity because of the more adsorbate–adsorbent interaction probabilities. Also, the existence of surface functionalities in the adsorbent helps in the adsorption of certain target molecules/compounds. Nonetheless, adsorption is a unique process that relies upon not only the physicochemical properties of the adsorbent (e.g. specific surface, pore size, surface chemistry, etc.) alone but also on the inherent characteristics of the adsorbate (e.g. molecular size, polarity, charge density, steric hindrance, etc.) and the environment or operating conditions (e.g. temperature, concentration, retention time, co-existing substances, etc.) that bring about the affinity of adsorbate–adsorbent interactions and mechanisms, such as π-π, hydrogen bonding, pore filling, electrostatic, ion-exchange, etc.

The application of adsorption mechanisms to the removal of impurities encounters an advanced breakthrough when the artificial zeolite was formulated, and operation cycles are designed to recover product and regenerate used adsorbents. Every system including an adsorption process performs two critical actions: the separation of one or more substances with higher affinity and the regeneration of spent adsorbents from the adsorbent bed. These two procedures can be carried out in a continuous sequence or in a parallel multi-bed setup, with no adsorbents being wasted. The newly regenerated adsorbents are reused in cycles, and the adsorbate is recovered at the same time [39].

4.2 Methylene blue and Congo red adsorption

Methylene blue is a cationic dye that is poisonous and carcinogenic if accidentally ingested, whereas Congo red is an anionic dye that can have a serious impact on aquatic living organisms if discharged into the aquatic environment from industry effluent [40]. Therefore, it is important to separate these dyes from the industry effluent and the water bodies. Surface area, initial concentration, contact time, pH, and adsorption temperature are some parameters that influence the adsorption capacity of dyes. The adsorption of methylene blue and Congo red by various activated carbons is illustrated in *Table 3*. The number of active sites, porosity, and pore volume of the adsorbent facilitate the removal of dyes through several synergistic interactions. Meanwhile, an increase in temperature reduces solution viscosity and gives dye molecules more kinetic energy, increasing their mobility and diffusion onto the surface of the adsorbent and the internal pores, resulting in enhanced dye uptake [41].

Likewise, when the initial concentration of the dye increases, the quantity of the molecules absorbed per unit mass of the adsorbent also increases. For instance, the adsorption capacity of methylene blue by rubber-sludge-based activated carbon increases from 224 to 458 mg/g when the initial concentration increased from 250 to 500 mg/L. Similarly, the capacity of Congo red removal using sargassum-based activated carbon increases from 125.66 to 234.00 mg/g when the initial concentration increased from 100 to 200 mg/L. The concentration gradient offers a driving force to facilitate dye diffusion from bulk solution onto the adsorbent. In the case of activated carbon, the contact time is adjusted depending on the initial concentration, as a longer contact time to attain equilibrium is required for a higher initial concentration [42].

Table 3. Adsorption of methylene blue and Congo red by various adsorbents.

Adsorbent	Dye	BET area (m2/g)	Concentration (mg/L)	Contact time (T, °C), [pH]	Capacity (mg/g)	Removal (%)	Reference
Banana-stem-based activated carbon	Methylene blue	837	100	90 min, [7]	101	99.8	[43]
Mangosteen-peel-based activated carbon	Methylene blue	1,832	500	5 h, (25°C), [7]	871	–	[44]
Oil-palm-based activated carbon	Methylene blue	553	50	2 h, [3]	24	48	[45]
Rubber-sludge-based activated carbon	Methylene blue	-	250 500	2 h, (30°C), [5]	224 458	94.8	[46]
Tea-waste-based activated carbon	Methylene blue	851	500	-	357	71.4	[47]
Palm-shell-based activated carbon	Methylene blue	1,038	55	50 min, [10]	51.50	91.8	[48]
Kenaf-based activated carbon	Congo red	843	25	2 h, (27°C), [4]	19.7	78.9	[49]
Myrtus-communis-based activated carbon	Congo red	104	30	-	19.2	64.1	[50]
Orange-peel-based activated carbon	Congo red	1,169	750	2 h, (35°C), [4]	667	88.9	[51]
Casuarina-empty-fruit-based activated carbon	Congo red	1,072	300	144 h, (25°C)	232	77.3	[52]
Sargassum-fusiforme-based activated carbon	Congo red	1,329	100 200	3 h, (50°C), [7]	126 234	94.7	[53]
Walnut-shell-based activated carbon	Congo red	800	200	9 h, (25°C)	154	77	[54]

5. Conclusions

Dyes are toxic and recalcitrant to biodegradation. Methylene blue and Congo red are among the widely used dyes in industries. Therefore, there is an urgency to treat effluent laden with dyes prior to be discharged to the environment. In this mini-review, we highlighted recent works on methylene blue and Congo red adsorption by activated carbons. Synergistic interactions in terms of the physicochemical properties of the adsorbent, the intrinsic characteristics of dye, and the adsorption environment are expected to result in favourable adsorbate–adsorbent interactions in wastewater treatment.

Acknowledgements

This work was supported in part by UTM-ICONIC Grant No. 09G54.

References

[1] Woodhead, A. L., Cosgrove, B., Church, J. S. (2016), The purple coloration of four late 19th century silk dresses: A spectroscopic investigation. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* 154, 185–192.

[2] Pearce, C. (2003), The removal of colour from textile wastewater using whole bacterial cells: A review. *Dyes Pigm.* 58(3), 179–196.

[3] Nikravesh, B., Shomalnasab, A., Nayyer, A., Aghababaei, N., Zarebi, R., Ghanbari, F. (2020), UV/chlorine process for dye degradation in aqueous solution: Mechanism, affecting factors and toxicity evaluation for textile wastewater, *J. Environ. Chem. Eng.* 8(5), 104244.

[4] Abe, F. R., Machado, A. L., Soares, A., Oliveira, D. P., Pestana, J. L. T. (2019), Life history and behavior effects of synthetic and natural dyes on Daphnia magna. *Chemosphere* 236, 124390.

[5] Khatri, A., Peerzada, M. H., Mohsin, M., White, M. (2015), A review on developments in dyeing cotton fabrics with reactive dyes for reducing effluent pollution. *J. Clean. Prod.* 87, 50–57.

[6] Wainwright, M. (2008), Dyes in the development of drugs and pharmaceuticals. *Dyes Pigm.* 76(3), 582–589.

[7] Benkhaya, S., M'rabet, S., El-Harfi, A. (2020), A review on classifications, recent synthesis and applications of textile dyes. *Inorg. Chem. Commun.* 115, 107891.

[8] Hassan, M. M., Carr, C. M. (2021), Biomass-derived porous carbonaceous materials and their composites as adsorbents for cationic and anionic dyes: A review. *Chemosphere* 265, 129087.

[9] Liu, D., Gu, W., Zhou, L., Wang, L., Zhang, J., Liu, Y., Lei, J. (2022), Recent advances in MOF-derived carbon-based nanomaterials for environmental applications in adsorption and catalytic degradation. *Chem. Eng. J.* 427, 131503.

[10] Parmar, M., Sanyal, M. (2022), Extensive study on plant mediated green synthesis of metal nanoparticles and their application for degradation of cationic and anionic dyes. *Environ. Nanotechnol. Monit. Manag.* 17, 100624.

[11] Penthala, R., Oh, H., Park, S. H., Lee, I. Y., Ko, E. H., Son, Y.-A. (2022), Synthesis of novel reactive disperse dyes comprising carbamate and cyanuric chloride groups for dyeing polyamide and cotton fabrics in supercritical carbon dioxide. *Dyes Pigm.* 198, 110003.

[12] Delport, A., Harvey, B. H., Petzer, A., Petzer, J. P. (2017), The monoamine oxidase inhibition properties of selected structural analogues of methylene blue. *Toxicol. Appl. Pharmacol.* 325, 1–8.

[13] Shahinyan, G. A., Amirbekyan, A. Y., Markarian, S. A. (2019), Photophysical properties of methylene blue in water and in aqueous solutions of dimethylsulfoxide. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* 217, 170–175.

[14] Gensini, G. F., Conti, A. A., Lippi, D. (2007), The contributions of Paul Ehrlich to infectious disease. *J. Infect.* 54(3), 221–224.

[15] Burhenne, J., Riedel, K. D., Rengelshausen, J., Meissner, P., Muller, O., Mikus, G., Walter-Sack, I. (2008), Quantification of cationic anti-malaria agent methylene blue in different human biological matrices using cation exchange chromatography coupled to tandem mass spectrometry. *J. Chromatogr. B Analyt. Technol. Biomed. Life Sci.* 863(2), 273–282.

[16] Grauman-Neander, N., Loner, C.A., Rotoli, J. M. (2018), The acute treatment of methemoglobinemia in pregnancy. *J. Emerg. Med.* 54(5), 685–689.

[17] Liu, S., Ge, H., Wang, C., Zou, Y., Liu, J. (2018), Agricultural waste/graphene oxide 3D bio-adsorbent for highly efficient removal of methylene blue from water pollution. *Sci. Total Environ.* 628/629, 959–968.

[18] Steensma, D. P. (2001), Congo red: Out of Africa? *Arch. Pathol. Lab. Med.* 125, 250–252.

[19] Zheng, Y., Cheng, B., Fan, J., Yu, J., Ho, W. (2021), Review on nickel-based adsorption materials for Congo red. *J. Hazard. Mater.* 403, 123559.

[20] Howie, A. J., Brewer, D. B. (2009), Optical properties of amyloid stained by Congo red: History and mechanisms. *Micron.* 40(3), 285–301.

[21] Naseem, K., Farooqi, Z. H., Begum, R., Irfan, A. (2018), Removal of Congo red dye from aqueous medium by its catalytic reduction using sodium borohydride in the presence of various inorganic nano-catalysts: A review. *J. Clean. Prod.* 187, 296–307.

[22] Sun, G., Zhang, J., Hao, B., Li, X., Yan, M., Liu, K. (2022), Feasible synthesis of coal fly ash based porous composites with multiscale pore structure and its application in Congo red adsorption. *Chemosphere* 298, 134136.

[23] Zeebaree, A. Y. S, Zeebaree, S. Y. S, Rashid, R. F., Zebari, O. I. H, Albarwry, A. J. S., Ali, A. F., Zebari, A. Y. S. (2022), Sustainable engineering of plant-synthesized TiO_2 nanocatalysts: Diagnosis, properties and their photocatalytic performance in removing of methylene blue dye from effluent. A review. *Curr. Opin. Green Sustain. Chem.* 5, 100312.

[24] Chowdhury, M. F., Khandaker, S., Sarker, F., Islam, A., Rahman, M. T., Awual, M. R. (2020), Current treatment technologies and mechanisms for removal of indigo carmine dyes from wastewater: A review. *J. Mol. Liq.* 318, 114061.

[25] Karimifard, S., Alavi Moghaddam, M. R. (2018), Application of response surface methodology in physicochemical removal of dyes from wastewater: A critical review. *Sci. Total Environ.* 640/641, 772–797.

[26] McYotto, F., Wei, Q., Macharia, D. K., Huang, M., Shen, C., Chow, C. W. K. (2021), Effect of dye structure on color removal efficiency by coagulation. *Chem. Eng. J.* 405, 126674.

[27] Subrahmanya, T. M., Widakdo, J., Mani, S., Austria, H. F. M., Hung, W.-S., Makari, H. K., Nagar, J. K., Hu, C.-C., Lai, J.-Y. (2022), An eco-friendly and reusable syringe filter membrane for the efficient removal of dyes from water via low pressure filtration assisted self-assembling of graphene oxide and SBA-15/PDA. *J. Clean. Prod.* 349, 131425.

[28] Wazir, M. B., Daud, M., Ali, F., Al-Harthi, M. A. (2020), Dendrimer assisted dye-removal: A critical review of adsorption and catalytic degradation for wastewater treatment. *J. Mol. Liq.* 315, 113775.

[29] Joseph, J., Radhakrishnan, R. C., Johnson, J. K., Joy, S. P., Thomas, J. (2020), Ion-exchange mediated removal of cationic dye-stuffs from water using ammonium phosphomolybdate. *Mater. Chem. Phys.* 242, 122488.

[30] Azbar, N., Yonar, T., Kestioglu, K. (2004), Comparison of various advanced oxidation processes and chemical treatment methods for COD and color removal from a polyester and acetate fiber dyeing effluent. *Chemosphere* 55(1), 35–43.

[31] Elbatea, A. A., Nosier, S. A., Zatout, A. A., Hassan, I., Sedahmed, G. H., Abdel-Aziz, M. H., El-Naggar, M. A. (2021), Removal of reactive red 195 from dyeing wastewater using electro-Fenton process in a cell with oxygen sparged fixed bed electrodes. *J. Water Process Eng.* 41, 102042.

[32] Xin, Y.-Y., Zhou, L., Ma, K.-K., Lee, J., Qazi, H.I.A., Li, H.-P., Bao, C.-Y., Zhou, Y.-X. (2020), Removal of bromoamine acid in dye wastewater by gas-liquid plasma: The role of ozone and hydroxyl radical. *J. Water Process Eng.* 37, 101457.

[33] Mahmoodi, M., Rafiee, E., Eavani, S. (2022), Photocatalytic removal of toxic dyes, liquorice and tetracycline wastewaters by a mesoporous photocatalyst under irradiation of different lamps and sunlight. *J. Environ. Manage.* 313, 115023.

[34] Singh, A., Pal, D. B., Mohammad, A., Alhazmi, A., Haque, S., Yoon, T., Srivastava, N., Gupta, V. K. (2022), Biological remediation technologies for dyes and heavy metals in wastewater treatment: New insight. *Bioresour. Technol.* 343, 126154.

[35] Robens, E. (1994), Some intriguing items in the history of adsorption. *Studies in Surface Science and Catalysis* 87, 109–118.

[36] Bensalah, J., Benhiba, F., Habsaoui, A., Ouass, A., Zarrouk, A., Lebkiri, A., El-Khattabi, O., Rifi, E. H. (2022), The adsorption mechanism of the anionic and cationic dyes of the cationic resin A®IRC-50, kinetic study and theoretical investigation using DFT. *J. Indian Chem. Soc.* 99(7), 100512.

[37] Geca, M., Wisniewska, M., Nowicki, P. (2022), Biochars and activated carbons as adsorbents of inorganic and organic compounds from multicomponent systems – A review. *Adv. Colloid Interface. Sci.* 305, 102687.

[38] Babatunde, K. A., Negash, B. M., Jufar, S. R., Ahmed, T. Y., Mojid, M. R. (2022), Adsorption of gases on heterogeneous shale surfaces: A review. *J. Pet. Sci. Eng.* 208(B), 109466.

[39] Sultana, M., Rownok, M. H., Sabrin, M., Rahaman, M. H., Alam, S. M. N. (2022). A review on experimental chemically modified activated carbon to enhance dye and heavy metals adsorption. *Clean. Eng. Tech.* 6, 100382.

[40] Bal, G., Thakur, A. (2022), Distinct approaches of removal of dyes from wastewater: A review. *Mater. Today Proc.* 50, 1575–1579.

[41] Rashid, S., Shen, C., Yang, J., Liu, J., Li, J. (2018), Preparation and properties of chitosan-metal complex: Some factors influencing the adsorption capacity for dyes in aqueous solution. *J. Environ. Sci.* 66, 301–309.

[42] Osagie, C., Othmani, A., Ghosh, S., Malloum, A., Kashitarash Esfahani, Z., Ahmadi, S. (2021), Dyes adsorption from aqueous media through the nanotechnology: A review. *J. Mater. Res. Tech.* 14, 2195–2218.

[43] Misran, E., Bani, O., Situmeang, E. M., Purba, A. S. (2022), Banana stem based activated carbon as a low-cost adsorbent for methylene blue removal: Isotherm, kinetics, reusability. *Alex. Eng. J.* 61(3), 1946–1955.

[44] Zhang, Z., Xu, L., Liu, Y., Feng, R., Zou, T., Zhang, Y., Zhou, P. (2021), Efficient removal of methylene blue using the mesoporous activated carbon obtained from mangosteen peel wastes: Kinetic, equilibrium, thermodynamic studies. *Microporous Mesoporous Mater.* 315, 110904.

[45] Baloo, L., Isa, M. H., Sapari, N. B., Jagaba, A. H., Wei, L. J., Yavari, S., Razali, R., Vasu, R. (2021), Adsorptive removal of methylene blue and acid orange 10 dyes from aqueous solutions using oil palm wastes-derived activated carbons. *Alex. Eng. J.* 60(6), 5611–5629.

[46] Mahapatra, U., Manna, A. K., Chatterjee, A. (2022), A critical evaluation of conventional kinetic and isotherm modeling for adsorptive removal of hexavalent chromium and methylene blue by natural rubber sludge-derived activated carbon and commercial activated carbon. *Bioresour. Technol.* 343, 126135.

[47] Tuli, F. J., Hossain, A., Kibria, A. K. M. F., Tareq, A. R. M., Mamun, S. M. M. A., Ullah, A. K. M. A. (2020), Removal of methylene blue from water by low-cost activated carbon prepared from tea waste: A study of adsorption isotherm and kinetics. *Environ. Nanotechnol. Monit. Manag.* 14, 100354.

[48] Muniyandi, M., Govindaraj, P., Bharath-Balji, G. (2021), Potential removal of methylene blue dye from synthetic textile effluent using activated carbon derived from palmyra (palm) shell. *Mater. Today Proc.* 47, 299–311.

[49] Mandal, S., Calderon, J., Marpu, S. B., Omary, M. A., Shi, S. Q. (2021), Mesoporous activated carbon as a green adsorbent for the removal of heavy metals and Congo red: Characterization, adsorption kinetics, isotherm studies. *J. Contam. Hydrol.* 243, 103869.

[50] Ghaedi, M., Tavallali, H., Sharifi, M., Kokhdan, S. N., Asghari, A. (2012), Preparation of low cost activated carbon from myrtus communis and pomegranate and their efficient application for removal of Congo red from aqueous solution. *Spectrochim. Acta, Part A: Mol. Biomol. Spectrosc.* 86, 107–114.

[51] Karaman, C., Karaman, O., Show, P. L., Karimi-Maleh, H., Zare, N. (2022), Congo red dye removal from aqueous environment by cationic surfactant modified-biomass derived carbon: Equilibrium, kinetic, thermodynamic modeling, forecasting via artificial neural network approach. *Chemosphere* 290, 133346.

[52] Amran, F., Zaini, M. A. A. (2021), Valorization of casuarina empty fruit-based activated carbons for dyes removal – Activators, isotherm, kinetics and thermodynamics. *Surf. Interfaces* 25, 101277.

[53] Ma, M., Ying, H., Cao, F., Wang, Q., Ai, N. (2020), Adsorption of Congo red on mesoporous activated carbon prepared by CO_2 physical activation. *Chin. J. Chem. Eng.* 28(4), 1069–1076.

[54] Li, Z., Hanafy, H., Zhang, L., Sellaoui, L., Schadeck Netto, M., Oliveira, M. L. S., Li, Q. (2020), Adsorption of Congo red and methylene blue dyes on an ashitaba waste and a walnut shell-based activated carbon from aqueous solutions: Experiments, characterization and physical interpretations. *Chem. Eng. J.* 388, 124263.