CHAPTER 3 ENVIRONMENTAL AREA

MESOPOROUS SILICA NANOPARTICLES AS ADSORBENTS OF METHYLENE BLUE AQUEOUS SOLUTIONS

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Abstract

Methylene blue (MB) is one of the most popular cationic dyes that is environmentally persistent. It has several uses in industry such as synthetic dye for dyeing fabrics in clothing, textile industries and for dyeing paper and leathers. However, the periodical use of dyes generates waste, wastewater is one of the most worrying problems, not only because it can cause detrimental health issues for humans but because it can be a source of damage to the environment. Thus, it is highly necessary to eliminate MB dye from wastewater. Various methods are reported to remove MB and other textile dyes of water. The adsorption method is one of the most used methods to remove MB of contaminated water. Nanomaterials such as mesoporous silica nanoparticles have been used as adsorbents for dyes showing excellent results. This work discusses the risks posed by water contaminated with MB, as well as the most used methods for the removal of this dye, highlighting the adsorption method and mesoporous silica nanoparticles as adsorbents. In addition, presents a study of these nanostructure's efficiency as methylene blue adsorbents.

Keywords: Methylene blue dye; Mesoporous Silica nanoparticles; Optical properties.

1. Introduction

Access to drinking water is crucial for the community and fundamental for economic and social development. However, urban growth and industrialization have negatively affected this resource. According to a report from the Organization for Economic Cooperation and Development (OECD, 2017), the textile industry stands out as one of the largest consumers of water [1].

The use of dyes is prevalent in several industries, including textiles, pharmaceuticals, food and cosmetics, among others. However, the textile industry is mainly responsible for dye pollution, since it is estimated that between 10% and 15% of the dyes used in its processes end up contaminating the environment [2].

According to the Scopus database, MB is widely used in various applications. From 2014 to 2023, the number of articles on MB dye degradation has increased steadily, as shown in Figure 1.

Figure 1. Graphic of articles per year for methylene blue removing.

Methylene blue (MB) is one of the most used materials in the dye industry, being commonly used to dye silk, wool, cotton and paper [3]. The presence of MB in water, even at low concentrations, can reduce sunlight transmission, decrease oxygen solubility, affect the photosynthetic activity of aquatic organisms, and reduce the diversity and aesthetics of biological communities [4].

It is crucial to implement strategies to remove methylene blue from contaminated water as soon as possible. Until now, some of the most widely used methods include biological methods (using microorganisms), chemical methods (using advanced oxidation processes), and physicochemical methods (such as adsorption). With the advancement of nanotechnology in various scientific areas, some nanomaterials have been proposed as dye adsorbents, obtaining positive results in their elimination. Mesoporous silica nanoparticles are applicable in areas such as adsorption, catalysis, and electrochemistry, due to their large specific surface area, porous structure, and numerous functional groups on their surface [5].

This article discusses the damage that can be caused by water contaminated with methylene blue to the environment and to humans, as well as the use of silica mesoporous nanoparticles as adsorbents.

1.1. *Methylene Blue Dye*

Dyes are molecules that have great resistance to biodegradation due to their organic and inorganic compounds [6]. These dyes have various applications in industry and are generally classified as anionic, cationic and nonionic. Methylene blue (MB) was first synthesized by Heinrich Caro in 1800 [7 - 10]. MB is a cationic dye, with the molecular formula $C_{16}H_{18}N_3ClS$, and has maximum absorption in the visible region. It is highly soluble in water, forming a stable solution at room temperature [11, 12]. MB acts as a redox indicator, not as a pH indicator [13]. The chemical structure of the MB molecule is shown in Figure 2.

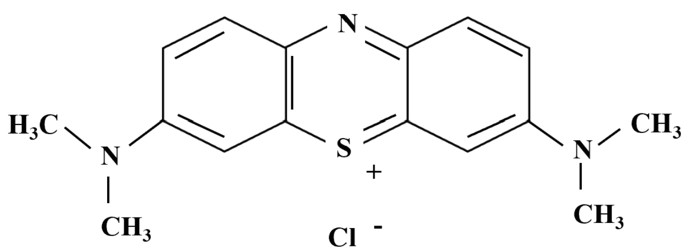

Figure 2. The chemical structure of methylene blue molecule.

The absorption spectra of methylene blue (MB) show a more intense absorption peak around 664 nm, associated with its monomer, and a signal around 612 nm, attributed to its dimer. Furthermore, in the ultraviolet region, two additional bands are observed around 290 and 245 nm, corresponding to benzene rings [14]. Due to its high molar absorption coefficient, approximately

8×10^4 L mol^{-1} cm^{-1} at 664 nm [15], this region of highest absorption is optimal for determining the presence of this dye in water.

1.2. *Toxicity of Methylene Blue Dye*

Wastewater generated by industries, which is often dumped near lakes or rivers, not only damages the ecosystem but also affects human health. Methylene blue (MB), in certain concentrations, can be considered toxic and cause irreversible damage to health [16]. MB can cause dermatological, central nervous system, gastrointestinal and cardiovascular diseases (see Figure 3)

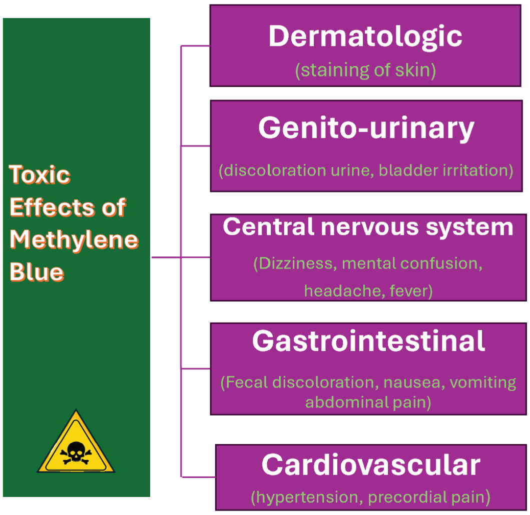

Figure 3. Toxic effects of methylene blue of exposure of methylene blue in humans [17].

Contact of methylene blue (MB) with the skin can cause spots and itching. Additionally, it can cause discoloration of urine, bladder irritation, dizziness, mental confusion, headaches, and fever. In the gastrointestinal system, MB can cause abdominal pain, nausea, vomiting, and discoloration of stool. Cardiovascular problems, such as hypertension and chest pain, have also been reported due to exposure to methylene blue [17].

The damage that this dye can cause not only to the environment, but also the negative effects it has on health, requires methodologies that eliminate or remove the highest possible concentration of methylene blue contained in wastewater.

1.3. *Removal Methods of Methylene Blue*

The removal of dyes from water is a major problem due to the difficulty of treating this type of wastewater with conventional methods. There are various techniques for dye removal, including photocatalytic degradation, adsorption, membrane filtration, biological degradation, microwave catalysis, and oxidation [18].

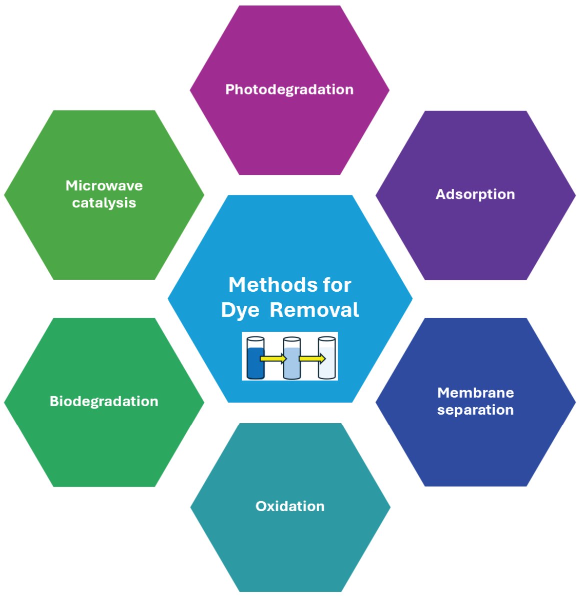

Figure 4. Methods for dye removal.

The removal of dyes through photocatalysis is considered a viable technology at an industrial level. This photocatalytic degradation process is based on the production of highly reactive radicals, such as photographically generated hydroxyl and superoxide anions, which attack the dye molecules and completely mineralize them into less harmful species, such as CO_2 and H_2O [19]. However, the main challenge of photocatalytic degradation of pollutants in wastewater is the long time required and the difficulty in recovering the photocatalysts. Microwave catalytic degradation involves ion conduction. When a catalyst is exposed to microwave radiation, a uniform superheating action is generated [20]. Achieving uniform heating throughout the reaction mixture can be difficult. Biological treatment has several advantages, such as its simplicity, low cost, and being an environmentally friendly process. Additionally, there are many microorganisms available that are easy to maintain and require little preparation [21]. However, this method requires careful optimization and monitoring. Membrane separation technology offers both the removal and recovery of synthetic dyes from wastewater, representing a promising avenue in engineering [22]. However, in membrane filtration techniques, the decrease in flow rate due to membrane clogging is a problem, along with the complexity and high cost in manufacturing the membranes.

1.4. *The Absorption Method*

The adsorption method for the removal of dyes, such as methylene blue, uses solid sorbents. Recently, this process has become one of the most effective and attractive for the treatment of wastewater containing dyes. In this process, liquid contaminants adhere to the surface of a solid, and it is considered one of the most advanced technologies for water treatment due to its low cost, sustainability and ease of use [23]. A notable feature of this technology is that it does not generate secondary pollutants and does not require complicated setup or operating costs. Compared to technologies such as chemical oxidation, membrane technologies and biological treatment processes that involve the generation of toxic sludge, extensive setup operations are not cost-effective [24].

The adsorption mechanism can be physical or chemical, depending mainly on the aromatic and/or functional groups present in the organic contaminants. Physical adsorption involves weak interactions, such as van der Waals forces, between the adsorbate and the adsorbent. On the other hand, chemical adsorption occurs when chemical bonds form between the adsorbate and specific functional groups on the surface of the adsorbent [25].

Nanomaterials have become one of the most applicable materials for adsorption, thanks to their versatility and nanoscale properties, which makes them extremely useful. Silica nanoparticles have attracted significant attention as nanoadsorbents due to their regular structural characteristics, larger surface area, tunable pore diameters, good thermal and chemical stability, and ease of surface modification [26]. Mesoporous silica nanoparticles (MSNs) are porous materials that have been widely chosen as adsorbents due to their unique surface and pore properties as well as their high surface area [27]. The adsorption of dyes on MSNs is carried out both by chemical interactions and by their porous properties. In general, the functional group on the surface of MSNs is the hydroxyl group, which can interact with the active sites of dye molecules [28].

1.5. *Mesoporous Silica Nanoparticles as Adsorbent Dyes*

Mesoporous silica nanoparticles have become one of the nanomaterials with the greatest variety of applications due to their morphological characteristics, such as their variable size, large surface area (more than 700 m^2), adjustable pore size, surfaces that are easy to functionalize and biocompatibility [29]. MSNs have significant applications in various research fields, including catalysis, adsorption, separation, detection and release of drugs [30]. Mesoporous materials are generally prepared using self-assembled surfactant molecules as templates around which silica precursors condense [31]. The template is then removed by heat treatment, resulting in a porous material. By varying conditions such as temperature, pH, surfactant concentration, pore size and morphology, these characteristics can be controlled

There are several synthesis methods for MSNs, such as the sol-gel method, the microwave-assisted technique and chemical etching. However, the sol-gel method is widely used due to its ease and the uniform and controllable growth of nanoparticles. The Stöber method involves the hydrolysis and condensation of tetraethyl orthosilicate (TEOS) in the presence of water and a basic catalyst (ammonium hydroxide) at room temperature.

1.6. *Parameters Affecting Methylene Blue Adsorption by MSN*

1.6.1. Effect of particle size

Particle size in adsorption can be an important factor. In 2019, *S. Irudhaya Raj* **[21]** observed the adsorption efficiency of MSNs with sizes of 100, 200, and 500 nm. Analysis was performed for methyl orange (MO), bromocresol green (BCG), methylene blue (MB), and rhodamine B (RB). UV-Vis spectroscopy was used to verify the adsorption of the dyes. In all adsorption experiments, the decrease in absorbance maxima for MO, BCG, RB, and MB was analyzed at 464, 617, 561, and 661 nm, respectively. The analysis confirmed that only the anionic dyes were adsorbed by the 100 nm nanoparticles, while the cationic dyes were adsorbed by the 500 nm nanoparticles, and both types of dyes were adsorbed by the 250 nm nanoparticles. The study reported that the 100 nm MSNs had an absorption of 295.05 mg L^{-1} for MO and BCG, and 297.54 mg L^{-1} for MB; for the 250 nm MSNs, the adsorption of MO, BCG, RB and MB was 271 mg L^{-1}, 272 mg L^{-1}, 274 mg L^{-1} and 277 mg L^{-1}, respectively; and finally, the 500 nm MSNs had adsorption values of 286 mg L^{-1} for RB and 290 mg L^{-1} for MB.

The authors explain that the observed behavior can be attributed to the fact that in the 250 nm MSNs there was a partial removal of the surfactant layer, allowing the adsorption of both anionic and cationic dyes. On the other hand, for 100 nm MSNs, calcination was not sufficient to eliminate the surfactant layer, which maintained a positive surface charge. On the other hand, in the 500 nm MSNs, the surfactant layer was completely removed, leaving negatively charged silica particles.

1.6.2. Effect of experimental conditions on the removal efficiency of dyes

R. Chueachot [26], analyzed different parameters such as pH, adsorbent dose and contact time, which can optimize adsorption. The optimal pH for the removal of dyes from aqueous solutions highlights the role of pH in the surface charge of the adsorbent. The pH range was expanded from 1 to 3; At a pH of 3, a low adsorption rate was observed, which the author probably attributes to the positive charge of the surface, which decreases the amount of adsorbed dye. As the pH increases, the surface appears to become negative, and the adsorption rate increases.

The effect of adsorbent dosage on the removal of methylene blue (MB) was analyzed to determine the optimal amount of adsorbent required for effective adsorption of the dye in aqueous solutions. The dose variation was from 0.01 to 0.20 g for a concentration of 3 mg L^{-1}. It was observed that the adsorbed dose decreased with increasing adsorbent dose, which could be attributed to the overlap or aggregation of the adsorption sites, resulting in a decrease in the total surface area of the adsorbent available for the MB.

In relation to the contact time (the time during which the silica nanoparticles are in contact with the methylene blue solution), this can affect the adsorption kinetics independently of other experimental parameters. Starting from the same initial concentration (3 mg L^{-1}), the contact time varied from zero to 120 minutes. It was found that the amount of adsorbed methylene blue increased with the increase in contact time. The adsorption of MB by the MSNs stabilized after 30 minutes of contact; After this period, no notable increase in the process was observed. Therefore, the authors indicate that 30 minutes is the optimal contact time.

1.6.3. Effect of added materials on the removal efficiency of dyes

The development of functionalized mesoporous silica adsorbents with appropriate functional groups for dyes has been an area of recent interest. Ying Li [32] synthesized chitosan magnetic mesoporous silica nanoparticles with a diameter of 105 nm, which showed a saturated methylene blue adsorption capacity of 43.03 mg g^{-1}. This highlights the importance of their recycling and reuse, since this type of nanoparticle demonstrated high adsorption efficiency even after being used for up to 4 cycles.

Similarly, Yul Hong [33] synthesized small iron oxide nanoparticles embedded in mesoporous silica nanoparticles as a regenerative adsorbent for methylene blue. In this study, a comparison was made between SiO_2 and Fe-Oxide/SiO_2, reporting a greater adsorption capacity for the latter even after 4 cycles. The regeneration process of Fe-Oxide/SiO_2 indicated that iron oxide nanoparticles can catalyze the thermal degradation of adsorbed MB molecules, regenerating the adsorption sites, which can be applied to other cationic organic dyes.

1.7. *Photothermal Techniques for MSNs Characterization*

Photopyroelectric (PP) techniques have been used to characterize the thermo-optical properties of SiO_2 colloids [34]. The highly dispersive of these nanostructures need modulated light sources that can provide reliable results.

These techniques are characterized by using this intensity- modulated radiation for optical characterization of liquids at a fixed modulation frequency *f*. The material absorb the radiation and generates temperature fluctuations, also named thermal diffusions waves, and for detecting these waves is used a pyroelectric sensor [35, 36].

The experimental setup to measure the optical absorption coefficient is shown in Figure 5. In this, the liquid sample absorbs the modulated radiation that travels through an optical window until it reaches the sample and crosses it. According to the model of Beer-Lambert this is the optical absorption coefficient β. taking the appropriate limiting conditions and employing a mathematical model for heat diffusion [34], the pyroelectric signal for amplitude, expressed as a function of the sample thickness (L) is given by:

$$VL = Ce^{-\beta L}$$

On the other hand, the pyroelectric phase, , remains constant.

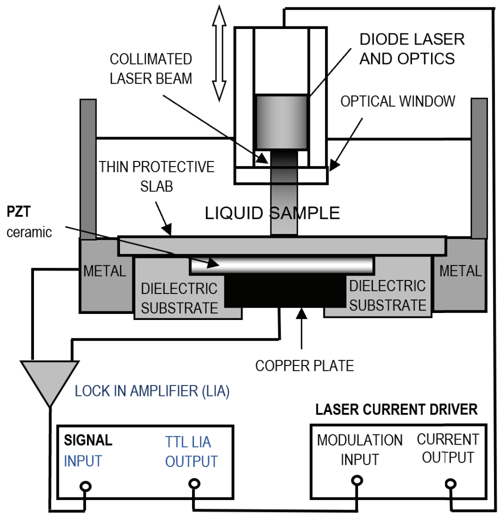

Figure 5. Cross section of the photopyroelectric setup for optical absorption coefficient measurements of liquids.

The slope of linear fit be the optical absorption coefficient for pyroelectrical amplitude as a function of the sample thickness (L) [37]. The constant phase is taken here as an experimental criterion to select a suitable range of sample thickness for reliable analysis.

2. Materials and Methods

The experiment consists of two phases, the synthesis of the MSNs and the testing of the effectiveness of these nanostructures as methylene blue adsorbents in aqueous solutions of different concentrations employing the Photopyroelectric techniques, to determine the optical absorption coefficient of each concentration.

2.1. *MSNs Synthesis*

The Stöber method reported by Ortiz-Islas [38] was used with some variations for the synthesis of MSNs. The reagents used were purchased from Sigma Aldrich. First 0.28 g of NaOH and 0.45 g of cetyltrimethylammonium ammonium bromide (CTAB) diluted in 479 mL of Milli-Q water were mixed, and then was heated at 70 °C. Subsequently 49 mL of Tetraethyl orthosilicate (TEOS at 98%) was added to the mixture. A dull white solution formed after mixing for 2 hours. Finally, the sample was calcinated at 550 ^{0}C to remove the CTAB.

2.2. *MSNs adsorption efficiency*

To probe the MSNs adsorption capacity different solutions of methylene blue at various concentrations (0.025, 0.05 and 0.1 mM) were elaborated. Then 5 ml of solution was taken apart and 0.01g of MSN were added, for later stirring for 35 min to enhance pigment's adsorption to the nanoparticles [26]. The samples were centrifuged at 10,000 rpm for 12 min until achieved the MSN precipitation. The MSNs precipitated was redispersed in 5 ml of milli Q water, to bring the volume closer to the initial volume after the dye's remotion. Finally optical absorption coefficients for the original suspension, the MSN resuspended and the supernatant were measured to determine the adsorption efficiency.

3. Results and discussion

Figure 6 shows the silica mesoporous nanoparticles synthetized in this work. The average size reported by Transmission Electron Microscopy (TEM, JEM1010, Japan) was 95 ± 12 nm.

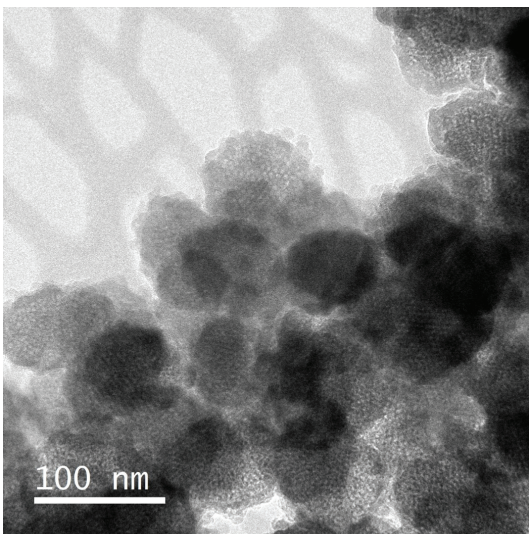

Figure 6. Micrography TEM of MSNs synthetized.

In Figure 7 is shown the optical absorption coefficient for different concentration of dye solutions at a wavelength of 660 nm. An excellent linear correlation is evident in the case between the absorption coefficient values and the increase of concentration samples. The results indicate that for these samples

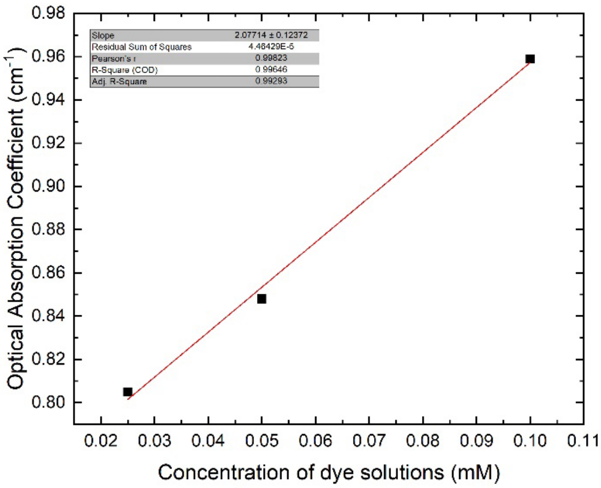

Figure 7. Micrography TEM of MSNs synthetized.

the Beer-Lambert law is fulfilled, which suggests that the optical characterization of this type of nanostructure to measure the adsorption efficiency by the absorption coefficient is reliable. The slope of the linear fit for the optical absorption coefficients with concentration corresponds to the absorptivity of the MSNs "loaded" with the MB dye, which resulted in a value of ε (660 nm) = 2.1 cm^{-1}/mM.

4. Conclusions

This article reports the toxicity of methylene blue, as well as the various strategies to remove this organic dye from contaminated waters. The adsorption method is easy to use due to its simplicity, low cost and sustainability. Nanomaterials are ideal as adsorbents, especially mesoporous silica nanoparticles (MSN), since, as observed by using photothermal techniques for optical characterization, it is possible to determine the adsorption efficiency of methylene blue of these nanoparticles.

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