Chapter 5

Use of Cellulosic Materials as Dye Adsorbents — A Prospective Study

Fabrícia C. Silva, Luciano C.B. Lima, Roosevelt D.S. Bezerra, Josy A. Osajima and Edson C. Silva Filho

Additional information is available at the end of the chapter

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Abstract

Cellulose is the most abundant biopolymer of nature, and it is widely used in the synthesis of new materials as well as in the adsorption of dye. This study reports a literature review (articles) and technology review (patents) about publications and product invention, which contain information on the use of cellulose on the adsorption of dyes in the period 2004–2014. For this work, research database and keywords were used to find articles and patents related to the subject under review. Specific words were used to find articles and patents related to the subject under review. After a demanding research, 1 patent and 23 articles that contain the words “cellulose,” “dye,” and “adsorption or sorption” in their titles were assessed, and annual evolution studies were performed for publications and countries that publish more.

Keywords: Cellulose, adsorption, dye, review, prospection

1. Introduction

One of the negative consequences of human development is the large amount of waste discharged into water bodies, with varied compositions that may contain heavy metals, dyes, and/or other undesirable chemical compounds [1, 2].

The problem becomes more serious when it comes to textile industrial wastewater, as they are colorful, produced on a large scale, and do not always receive due treatment before being discharged into the environment, carrying various impurities [2, 3].

The aquatic environment coming into contact with these effluents has modified physical and chemical properties due to their color because such dyes become visible at concentrations up
to 1 mg L$^{-1}$, resulting in serious aesthetic problems until their toxicity, leading to hazards to human and animal health [2].

Contamination by dyes prevents the development of fish farming and recreation as well as influence the ecological equilibrium affecting the proliferation of aquatic plants by reducing photosynthetic activity caused by the difficulty passage of sunlight. Thus, the removal of these dyes becomes important environmentally [4, 5].

The removal of these dyes are not always easy because of its complex molecular structures that make them stable to light and heat and resistant to biodegradation [6].

Available wastewater treatment processes mainly involve ion exchange [7], chemical precipitation [8], chemical degradation [9], reverse osmosis [10], oxidation/chemical reduction [11], and adsorption [12].

Adsorption particularly stands out because of its high efficiency combined with low cost. It removes chemical pollutants, returning the natural transparency of the medium, and often enables reusing the reuse of the adsorbent. It is a process that is commonly reversible, where the regeneration of the adsorbent becomes possible, further cheapening the practice of this process, beside the use of natural waste in the trash [12, 13].

The adsorption using low-cost adsorbents is recognized as an effective and economical method for the decontamination of water. Because of this, many studies have been conducted employing the adsorption process using these adsorbents; among them, one can mention corn cob [14], sugarcane bagasse [15], banana peel [16], sawdust [17], wheat straw, [18], orange peel [19], water hyacinth roots [20], peanut hull [21], eucalyptus leaf [22], rice husk [23], corn kernel [24], coconut husk [25], apple pomace [26], and other cellulosic waste used in natural or modified surface [27].

Cellulose is a biopolymer considered as an almost inexhaustible source of raw materials, and it can be cited, as an example, as a promising natural material that has been extensively explored by researchers in the adsorption area. It is even more attractive when it makes modifications in its structure in order to improve their existing properties or adding new potentialities to this material [12, 28–30].

Modifying the surface of the cellulose can varies some of its properties, such as its hydrophilic or hydrophobic character, elasticity, resistance to microbiological attacks, and thermal and mechanical resistance, may also increase its pollutant adsorption capacity in aqueous and/or nonaqueous solutions [31].

The elucidation of the polymeric structure of cellulose was made by the pioneering work of Hermann Staudinger [32]. Through acetylation and deacetylation, he recognized that the structures did not consist merely of an aggregate of D-glucose units. Rather, glycosidic units were discovered by being linked covalently to one other to form long molecular chains.

Figure 1 shows the molecular structure of cellulose as a polymeric carbohydrate generated by β-D-glucopyranose repeating, which is covalently linked by acetal functions between the equatorial OH group of 4-carbon atom (C4) and the 1-carbon atom (C1). Hence, this resulted
in β-1,4-glucan denomination, which is in principle the way in which the cellulose is biogenetically formed. We have the cellulose as a straight-chain extended polymer with a large number of hydroxyl groups: three per anhydroglucose unit (AGU), which is the central unit, see Figure 1, a thermodynamically preferred conformation 4C1 bond between the 4-carbon and the 1-carbon [33].

![Cellulose molecular structure showing the numbering of the carbon atoms and functional groups per monomer of the polymer.](image)

This chapter aims to present a literature and technology review about the use of cellulosic materials in the adsorption of dyes, published and/or deposited during the period 2004 to 2014.

The prospection performed in this work was based on an extensive electronic search in patent databases and articles databases.

For prospecting patent, a search in the free databases available, that is, the European Patent Office (EPO), the National Institute of Industrial Property (INPI), and the United States Patent and Trademark Office (USPTO), was carried out. The keywords cellulose, cellulose and dye, cellulose and adsorption, cellulose adsorption, cellulose and adsorption and dye, and cellulose and sorption and dye were used to specify the search in the EPO and USPTO bases, and the related keywords in Portuguese were used for INPI, including “title.”

For the prospection of the articles, a survey was conducted to determine the most published database (Web of Science, Science Direct, Scopus, and Scielo) during the period 2004 to 2014. The same keywords used in the search of patents were used, including “title” and exclusively regular articles publications. Review articles, books, and book chapters were left out of the research. The research was conducted in April 2015. The articles found in database with largest amount of publication were subsequently analyzed.

2. Current state of the art in use of cellulosic materials as dye adsorbent

The investigation of patent by databases showed that the EPO was the database that received more product invention associated with the subject studied during the period investigated compared USPTO and INPI, as shown in Table 1.

Table 1 shows that when the more general term “cellulose” was used, the largest number of invention products in all databases was found. As new words are added and crossed, the
amount of invention products considerably decreased because the patents containing the word cellulose in their titles have many different purposes.

The patent only found in the databases after refinement was the German patent DE102008026403 (A1)—Dyeing cellulose fibres, e.g., cotton fabric, with reactive vinylsulfone dyes, involves adding dye-bath components in a special sequence to optimize the relation between physical adsorption and chemical reactivity, containing in its title the words “cellulose,” “adsorption,” and “dye.” This patent brings a dyeing method of cellulose fibers with reactive dyes, intending to optimize the relationship between physical adsorption and chemical reactivity in order to improve dye fixation on cellulose fiber [34].

In the prospection of articles, it was observed that the amount of published articles was higher compared to the number of patents, as shown in Table 2.

Table 1. Total patents registered on the databases EPO, USPTO, and INPI during the period 2004 to 2014.

<table>
<thead>
<tr>
<th>Keywords</th>
<th>EPO</th>
<th>USPTO</th>
<th>INPI</th>
</tr>
</thead>
<tbody>
<tr>
<td>cellulose</td>
<td>13,355</td>
<td>823</td>
<td>1</td>
</tr>
<tr>
<td>cellulose and dye</td>
<td>46</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>cellulose and adsorption</td>
<td>19</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>cellulose and sorption</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>cellulose and adsorption and dye</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>cellulose and sorption and dye</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>TOTAL</td>
<td>13,422</td>
<td>828</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 2. Number of articles published on Web of Science, Science Direct, Scopus, and Scielo databases from 2004 to 2014.

<table>
<thead>
<tr>
<th>Keywords</th>
<th>Cellulose</th>
<th>Cellulose and dye</th>
<th>Cellulose and adsorption</th>
<th>Cellulose and sorption</th>
<th>Cellulose and adsorption and dye</th>
<th>Cellulose and sorption and dye</th>
</tr>
</thead>
<tbody>
<tr>
<td>Web of Science</td>
<td>18,428</td>
<td>165</td>
<td>330</td>
<td>97</td>
<td>15</td>
<td>5</td>
</tr>
<tr>
<td>Science Direct</td>
<td>4,126</td>
<td>39</td>
<td>120</td>
<td>25</td>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td>Scopus</td>
<td>13,985</td>
<td>142</td>
<td>356</td>
<td>99</td>
<td>19</td>
<td>4</td>
</tr>
<tr>
<td>Scielo</td>
<td>154</td>
<td>0</td>
<td>7</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 2 shows that the database with the largest number of articles published in the area is Scopus, which showed higher publication when compared with other databases analyzed.

Observing the results obtained in this research using the database Scielo, articles related to the theme in the time period analyzed for their journals are not included. However, 8 articles related to the use of cellulosic materials for adsorption studies have been found. These articles
were aimed at removing other species that were not dye. This fact was confirmed when the words “cellulose” and “dye” were used, which were not found articles.

Thus, the research regarding the adsorption of the dye using cellulosic materials as adsorbents was evaluated by analyzing the 23 articles found in this database containing the words “cellulose, adsorption, and dye” and “cellulose, sorption, and dye” in their titles in the last 10-year period from 2004 to 2014.

Figure 2 shows the study of the annual evolution of publications.

![Figure 2. Annual evolution of articles published.](image)

This result proves that the adsorption of dyes using cellulosic material is a subject that is being currently studied, and the year 2013 showed the highest amount of publication about this topic, presenting a number of 7 from the 23 reviews.

Among the countries that published, China was ranked first, followed by the United Kingdom, India, and Iran, showing that the world’s major economies have shown interest in this study (Figure 3).

![Figure 3. Countries that more published articles.](image)
Adsorption studies often have the aim to evaluate the maximum removal capacity for a given compound (in this case dye) by adsorbent material proposed (in this case, the cellulosic materials). Moreover, there is a wide range of possibility in the variation of experimental parameters and conditions that directly influence in such property, or there are researchers who are concerned with elucidating the various existing mechanisms in this process, making use of theoretical models established or even proposing new theoretical models their investigations, often making use of computational tools.

Thus, it is observed that the publications about this theme can be divided into two major groups: the experimental conditions and parameters for the maximum removal capacity for a given dye and the theoretical studies to elucidate this process, explaining experimental data existing or proposed theoretical models that can be used in the elucidation of this process in general.

Analyzing the articles relating to this theme found in the Scopus database, note that of the 23 articles found (of which 19 articles were found with the keywords “cellulose,” “adsorption,” and “dye” and 4 items with words keys “cellulose,” “sorption,” and “dye”), 7 works bring theoretical studies to understand the adsorption process of given dyes on cellulosic materials or do not make use of parameter variation for study of maximum adsorption capacity for the material proposed, thus using different methodologies to other articles.

One of these studies is about reference [35], which brings the validation of proposed new nonlinear mathematical model of adsorption isotherm using a correlation between the classical data dye adsorption CI Direct Blue 1 in bleached cotton and the data obtained by the nonlinear model proposed, showing that the new model is presented with excellent results setting and brings the possibility of calculation of new parameters on the adsorption process.

The articles in references [36,37] made use of computational methods exploring the quantum mechanical method DFT/BPW91/6-31+G(d) using Gaussian 03 software and isotherm theoretical models for a better understanding of the interaction between adsorbent and adsorbate. These studies evaluated the effect of alkaline treatment using NaOH solutions of different concentrations of cellulose II fibers in the adsorption capacity for the Reactive Red 120 dye in the work of reference [36] and the dye CI Reactive Orange 84 and CI Reactive Red 120 [37].

In references [38,39], the authors published about the adsorption process of xanthene dyes on cellulose granules using a different methodology from other publications evaluated here, which made use of a method by column chromatography. Since the first work of Tabara et al. [38], they showed that the maximum adsorption capacity for the dyes erythrosine, rose bengal, and phloxine were 3.75, 3.42, and 4.74 mg g⁻¹, respectively. In their second study [39], they were concerned to elucidate the adsorption mechanism of such systems.

In article of reference [40], the authors have elucidated the structural factors that control the adsorption of acid dyes at the surface of cellulose; for this, they evaluated the adsorption of 15 different acid dyes on cellulose matrix, correlating with their structures and geometric values as the thermodynamic enthalpy and entropy of binding obtained in each process.

A theoretical and experimental study of the adsorption of a direct trisazo dye in mercerized cotton fiber, which use theoretical model by linear regression and nonlinear for the elucidation of such a process, was investigated in reference [41].
The remaining 15 articles have different methodologies, which aim at obtaining the maximum adsorption capacity for one or more dyes cellulose materials by investigating the influence of parameters such as pH, contact time, temperature, and others. Table 3 shows the main parameters obtained by this work, briefly specifying the proposed material as well as some of the values found for them. The main and most used parameters are better discussed, taking into regard the conclusions observed in these publications, in the following topics.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Dye</th>
<th>pH</th>
<th>Time</th>
<th>Temperature</th>
<th>Removal Capacity</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>carboxymethyl cellulose-acrylic acid</td>
<td>Methyl orange</td>
<td>&lt; 4.0</td>
<td></td>
<td>35 ºC</td>
<td>84.2%</td>
<td>[42]</td>
</tr>
<tr>
<td></td>
<td>Disperse blue</td>
<td>7.0</td>
<td>~40 min</td>
<td>45 ºC</td>
<td>79.6%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Malachite green</td>
<td>&gt; 9.0</td>
<td></td>
<td>40 ºC</td>
<td>99.9%</td>
<td></td>
</tr>
<tr>
<td>partially hydrolyzed polyacrylamide/cellulose nanocrystal</td>
<td>Methylene blue</td>
<td>5.0</td>
<td>240 min</td>
<td>-</td>
<td>326.08 mg g(^{-1})</td>
<td>[43]</td>
</tr>
<tr>
<td>Cellulose Agricultural Wastes</td>
<td>Violet B</td>
<td>11</td>
<td>90 min</td>
<td>-</td>
<td>96 mg g(^{-1})</td>
<td>[44]</td>
</tr>
<tr>
<td>microcrystalline cellulose gel/nano TiO(_2) composites</td>
<td>Methyl orange</td>
<td>-</td>
<td>30 min</td>
<td>-</td>
<td>94%</td>
<td>[45]</td>
</tr>
<tr>
<td>IPN Hydrogels based Carboxymethyl Cellulose</td>
<td>Basic fuchsin</td>
<td>-</td>
<td>-</td>
<td>25 ºC</td>
<td>2.249 mg g(^{-1})</td>
<td>[46]</td>
</tr>
<tr>
<td></td>
<td>Methyl violet</td>
<td>7</td>
<td>-</td>
<td>25 ºC</td>
<td>1.723 mg g(^{-1})</td>
<td></td>
</tr>
<tr>
<td>carboxymethyl cellulose/organic montmorillonite nanocomposites</td>
<td>Congo red</td>
<td>-</td>
<td>6 h</td>
<td>60 ºC</td>
<td>171.37 mg g(^{-1})</td>
<td>[47]</td>
</tr>
<tr>
<td>Bacterial Cellulose Plant Cellulose</td>
<td>Direct blue 71</td>
<td>3</td>
<td>120 min</td>
<td>30 ºC</td>
<td>25.15 mg g(^{-1})</td>
<td>[48]</td>
</tr>
<tr>
<td>Cellulose modified with quaternary ammonium groups</td>
<td>Reactive red 228</td>
<td>3</td>
<td>6 h</td>
<td>20 ºC</td>
<td>190.00 mg g(^{-1})</td>
<td>[49]</td>
</tr>
<tr>
<td>Cellulose modified with aminoethanethiol</td>
<td>Reactive red</td>
<td>2</td>
<td>100 min</td>
<td>55 ºC</td>
<td>78.00 mg g(^{-1})</td>
<td>[12]</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>160 min</td>
<td></td>
<td></td>
<td>26.00 mg g(^{-1})</td>
<td></td>
</tr>
<tr>
<td>Surface quaternized cellulose</td>
<td>Congo red</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>664.00 mg g(^{-1})</td>
<td>[50]</td>
</tr>
<tr>
<td></td>
<td>Acid green 25</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>683.00 mg g(^{-1})</td>
<td></td>
</tr>
<tr>
<td>Cellulose-based multicarboxyl</td>
<td>Malachite green</td>
<td>6</td>
<td>120 min</td>
<td>30 ºC</td>
<td>458.72 mg g(^{-1})</td>
<td>[51]</td>
</tr>
</tbody>
</table>
### Table 3. Adsorptive parameters used in articles according to prospection.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Dye</th>
<th>pH</th>
<th>Time</th>
<th>Temperature</th>
<th>Removal Capacity</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>adsorbent</td>
<td>Basic fuchsine</td>
<td>6.5</td>
<td>210 min</td>
<td></td>
<td>458.76 mg g⁻¹</td>
<td></td>
</tr>
<tr>
<td>Berinjal plant root powder (celulose)</td>
<td>Malachite green</td>
<td>6</td>
<td>35 mim</td>
<td>70 °C</td>
<td>100.29 mg g⁻¹</td>
<td>[52]</td>
</tr>
<tr>
<td></td>
<td>Methyl orange</td>
<td></td>
<td></td>
<td>40 °C</td>
<td>78.43 mg g⁻¹</td>
<td></td>
</tr>
<tr>
<td>Nano-cellulose hybrid</td>
<td>Yellow B-4RFN</td>
<td>7</td>
<td>240 mim</td>
<td>293 K</td>
<td>16.61 mg g⁻¹</td>
<td>[29]</td>
</tr>
<tr>
<td></td>
<td>Blue B-RN</td>
<td></td>
<td></td>
<td></td>
<td>14.40 mg g⁻¹</td>
<td></td>
</tr>
<tr>
<td>Magnetic cellulose beads</td>
<td>Methyl orange</td>
<td>-</td>
<td>180 min</td>
<td></td>
<td>0.045 mmol g⁻¹</td>
<td>[53]</td>
</tr>
<tr>
<td></td>
<td>Methylene blue</td>
<td></td>
<td></td>
<td></td>
<td>0.030 mmol g⁻¹</td>
<td></td>
</tr>
<tr>
<td>Modified cellulose with triazine derivatives</td>
<td>Reactive blue BF-RN</td>
<td>7</td>
<td>-</td>
<td>65 °C</td>
<td>20.00 mg g⁻¹</td>
<td>[30]</td>
</tr>
<tr>
<td>Unmodified cellulose</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>9.00 mg g⁻¹</td>
<td></td>
</tr>
</tbody>
</table>

2.1. Modification of cellulose

The presence of free hydroxyl on the surfaces of solids enables the application of a variety of reaction methods, which are explored to obtain new materials exhibited, due to the modification of their surfaces, new properties, or intensifying the existing ones, [54] not only in the reaction developing but also in applicability.

With regard specifically to cellulose, which is a renewable material and low cost, the reactivity is due to the hydroxyl groups, which are in an ideal position, with the primary hydroxyl at carbon 6 (C₆), much more reactive than secondary hydroxyl (C₂ and C₃). Although the reactivity of the hydroxyl depends heavily of the reagents and the reaction conditions, the hydroxyl group present at the 3-carbon is even less reactive. Thus, the cellulose hydroxyl groups have the following reactivity order: C₆ >> C₂ > C₃, this order being explained by the influence of the formation of inter- and intramolecular hydrogen bonds, as well as the degree of crystallinity, by favoring the water absorption in amorphous regions in comparison with the crystalline this material [55]. The main changes occurring in cellulose are due to halogenation, oxidation, etherification, and esterification.

Among the 23 articles found in the Scopus database, 12 present a proposal for the modification of cellulose aimed at intensification the properties of this biopolymer, a proof of importance of the modification of this promising material, to be involved in most of articles published in this area.

An example is the paper in reference [30], in which the authors modified cellulose incorporating cationic and anionic groups from the reaction with compounds of the triazine derivatives. With the proposed modification, the authors were able to increase the adsorption capacity for the reactive blue dye BF-RN, which was 9.00 mg g⁻¹ for a value of 20 mg g⁻¹ in an unmodified cellulose, justifying the proposed modification.
2.2. pH

The study of pH shows that the adsorption depends on the initial pH of the solution. The same process increases the maximum adsorption capacity because it distributes ions on the surface of the adsorbent by modifying their surface charge, and the dye molecules can be ionized, causing the interaction more efficient between adsorbent and adsorbate [56]. This study is very important (12 of 23 articles found on the prospection assessed the influence of this parameter in its work) and should always be performed in the adsorption tests because whether the pH will influence the adsorption process depends on the adsorbent and/or dye used.

Table 3 shows the reference [12] that evaluated the influence of pH on the reactive red dye adsorption on the surface of the modified cellulose with aminoethanethiol, and it presents the maximum adsorption capacity at pH 2 and pH 9. The authors explained that the maximum adsorption is favored by electrostatic interactions at pH 2 and by the formation of hydrogen bonds and/or covalent interactions with the adsorbent at pH 9.

Another study that verified the influence of this parameter is reference [49], which also studied the adsorption of reactive red dye. This work was conducted to modify the cellulose with incorporation of quaternary ammonium groups, with the aim of adding positive charges on their surface and thus improve the adsorption capacity.

It was observed that this material showed maximum adsorption capacity at pH 3. Considering that the dye molecules used in their studies have negative charges, the increase for dye removed at lower pH values than 6 is explained by favoring attraction electrostatic between dye and this adsorbent medium, cell-R-N-[C$_2$H$_5$]$_3$SO$_3^-$, but at pH values higher than 6, a decrease in the removal of dye different from the work described in reference [12] was noted. Due to the possibility of covalent interactions, they described good results at pH 9.

2.3. Contact time

Twelve of the 23 articles found in the prospection evaluated the influence of this parameter in its work, showing the importance of this parameter in the study of the adsorption process. By studying the influence of the adsorption contact time, it is possible to establish the adsorption equilibrium, which is reached when the adsorption capacity of the material remains constant over time. This study provides further data to establish the removal rate of the solute solution and how the adsorption takes place, making use of the kinetic studies that assess the theoretical model which best fit the experimental data.

The theoretical models for the kinetic study further reported in the literature are the pseudo-first order [57], the pseudo-second order [58], the intraparticle diffusion [59], and the Elovich equation [60].

In most of the articles investigated in the literature, it was observed that experimental data usually adjust better to the pseudo-second order kinetic model because the adsorption process is dependent on both the concentration of the adsorbate with the strength of the adsorbent [48, 52, 12, 51, 61, 62, 63].
An example of this is the work described in reference [29], in which the influence of contact time in the reactive adsorption of yellow dyes 4RFN B-B and reactive blue-NB in its hybrid material of cellulose showed that data fitted to the pseudo-second-order model. The authors of reference [51] also used this model to explain the adsorption of the dye malachite green and basic fuchsin since the experimental data showed a better linear correlation with the parameters of the pseudo-second-order model when compared to pseudo-first-order model.

The authors of reference [46] applied the mathematical models already mentioned and also used the kinetic model Bangham [64], but with a different objective from the other authors cited, as they have not sought the model with which the experimental data better adjusted but a comparison between linear and nonlinear form for each model. The results set is the best nonlinear models, based on the values of the statistical parameters.

2.4. Temperature

Studies on the temperature dependence of the dye adsorption process allow obtaining the experimental data enthalpy and entropy related to these processes. Among the evaluated articles, 12 related the study of the influence of temperature on the adsorption process.

The authors of reference [40] made use of this variable to understand the factors that control the adsorption process evaluating 15 different acid dyes cellulose adsorption. The authors observed the enthalpy of adsorption controls this process for most of dyes and came to the conclusion that the enthalpy of adsorption is controlled by the interaction of dye with the surface of material, i.e., a high enthalpy of adsorption will be observed the higher the approximation (permitted by the structure) of the aromatic nucleus of the dye to the material surface.

Given the dependence of the temperature in a range of 30°C to 70°C, the removal of malachite green dye methyl orange using brinjal plant root powder was evaluated in the paper [52]. For the first dye, the authors have observed an increase in the removal capacity by increasing the temperature, while for the second dye, the opposite trend was observed from 40°C. To explain these trends, the authors make use of the type of interaction between dyes and adsorbent.

The removal of the malachite green is explained by the interaction of the type of Lewis acid–base, thus increasing the temperature and the interaction between the charges of the basic sites of the material and the dye acids. However, in the adsorption of the anionic dye methyl orange, there are only interactions of the type of hydrogen bonds that can be broken easily at elevated temperatures according to the authors.

2.5. Dosage

In this study, 3 of the 23 articles found evaluated the dosage of the adsorbent. Despite the small number of studies among evaluated articles, the dosage of the adsorbent is another very important parameter because once the degree of the adsorption of a material under study is known, it is possible to use the optimal dosage of this adsorbent to determine, for example, the cost of the adsorbent per unit volume.
However, increasing the mass of adsorbent increases the amount of adsorption sites available for the adsorbent–adsorbate interactions on a qualitative analysis, resulting in the increased percentage of dye removal solution [65].

The paper of reference [46] confirmed this fact evaluating cellulose hydrogel dosage in the removal of basic fuchsin dye, finding a good dose of 1.0 g L\(^{-1}\); however, when the dose increased to 2.0 g L\(^{-1}\), the removal percentage continued to increase while the \(q_e\) value (mg g\(^{-1}\)) decreased.

In several reports, this factor is explained by the availability of sites for adsorption in the adsorbent because it is found to present limited fixed dye concentration and lower dosage, and therefore, each adsorbent achieves its maximum capacity. By contrast, at high dosages, the articles of adsorbent compete to bind the same dye molecules, thus providing a quantitative measure of the amount of adsorbed dye per unit weight of adsorbent decreasing [46, 62, 63].

2.6. Desorption

The possibility of recovery and reuse of biosorbent after going through a desorption process is another relevant factor. Five articles presented results in this parameter; two of them are described below.

The authors of reference [51] evaluated the life cycle of a new material obtained by the modification of cellulose with glycidyl methacrylate and diethylenetriaminepentaacetic acid, observing that, in their dynamic tests adsorption/desorption using a saturated solution of sodium bicarbonate as eluant, the adsorption capacity did not change significantly, showing that the material can be reused in at least four cycles, maintaining the adsorption rate above 85% and 90% for green and basic fuchsin dye malachite, respectively.

Another work that performed desorption testing is the paper of reference [53], in which we evaluated the life cycle of magnetic cellulose beads using NaCl solutions (2 mol L\(^{-1}\)) and NaOH (0.05 mol L\(^{-1}\)) and found that after three cycles of adsorption, the desorption was maintained at 95% for the dyes methylene blue and methyl orange, on this fact found that the beads can be reused several times.

The paper [52] also conducted a study of desorption, however, for the malachite green dye and methyl orange on the surface of brinjal plant root powder, and by just using water at 80°C, a recovery of 95% for methyl orange and 10% for malachite green was obtained.

The adsorption process involves several attractive interaction forces such as van der Waals forces, hydrogen bonding, covalent, and ionic bonds. Depending on the dye used and the sites available for adsorption on the material, one or more forces will act in the adsorption process, which influences the possibility to reuse the material.

3. Conclusion

Through the presented data, it can be stated that the use of cellulosic materials for the adsorption of dyes it is a promising area because of the number of publications found.
The data presented in the patent deposit prospecting shows the database with largest number of deposit among databases searched was EPO, with 12,815 patent deposits in studied range. Even though only a single patent occurs from the refined search referring to the aim of this study, it results in methods for improving fixation of the dye on cellulose fiber.

In the search for articles, a larger number of searches with limiting terms compared to prospecting patents were observed, in which China published more in this area. Other important aspects refer to the year in which most studies that have been done in this area, which was observed that the year 2013, had the highest number of publications showing currently of this theme.

The 23 items found in the Scopus database, using the limiting terms chosen, elucidate the adsorption of one or more dyes on the surface of cellulosic materials. By analyzing these articles, it can be proved that the factors influencing this process are pH, temperature, dosage, contact time, kind of material and modification. These parameters are of most importance in adsorption studies as well as in directly influencing the maximum adsorption capacity for a given material. Together they make an important tool in the elucidation of the possible interactions between adsorbent and adsorbate, helping to explain the potentiality of the material under study.

Author details

Fabrícia C. Silva¹, Luciano C.B. Lima¹, Roosevelt D.S. Bezerra², Josy A. Osajima¹ and Edson C. Silva Filho*¹

*Address all correspondence to: edsonfilho@ufpi.edu.br

1 LIMAV, Chemistry Department of Piauí Federal University, Teresina, Piauí, Brazil

2 Federal Institute of Education, Science and Technology of Piauí, Campus Teresina Central, Teresina, Brazil

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