Nanostructured MnO$_2$ catalyst in *E. crassipes* (water hyacinth) for indigo carmine degradation

**Abstract**

The use of water hyacinth’s dried matter (*Eichhornia crassipes*) as a support matrix for nano-MnO$_2$ and its application for the removal of indigo carmine (IC) was studied. Different pretreatment processes were tested and results indicated that an acid-alkali pretreatment is an efficient method to binding nanoparticles (NPs) to cellulosic matrix. In addition, the MnO$_2$ NPs were synthesized by sonochemical reduction of MnO$_2$$_5$ using different methods (ultrasonic horn system, ultrasonic bath and reaction with ethanol), where the influence of the precursor concentration was observed. The synthesized material was further characterized by ATR-IR, AAS, XRD, SEM, nitrogen isotherms adsorption, EDS, and pH$_{\text{pzc}}$. The IC removal capacity of the nanostructured material, the chemical nature of the degradation products and the effect of various parameters (temperature, pH, initial IC concentration, among others) were explored in water samples.

**Keywords:** *Eichhornia crassipes*, indigo carmine, nanostructured material, manganese oxide.

Catalizador de MnO$_2$ nanoestructurado en *E. crassipes* (jacinto de agua) para la degradación de indigo carmín

**Resumen**

Se estudió el uso de la materia seca del jacinto de agua (*Eichhornia crassipes*) como matriz de soporte para nano-MnO$_2$ y su eficiencia en la eliminación de indigo carmin (IC). Se ensayaron diferentes procesos de pretratamiento y los resultados indicaron que un tratamiento previo ácido-álcali es un método eficiente para unir las nanopartículas (NPs) a la matriz celulósica. Así mismo, las NPs de MnO$_2$ se sintetizaron por reducción sonoquímica de MnO$_2$$_5$ utilizando diferentes métodos (un sistema emisor de ultrasonido, ultrasonido y reacción convencional con etanol como medio). El material sintetizado fue caracterizado por ATR-IR, AAS, DRX, SEM, isómeras de adsorción de nitrógeno, EDS y pH$_{\text{pzc}}$. Se exploró la capacidad de eliminación de IC por parte del material nanoestructurado y la naturaleza química de los productos de degradación en muestras acuosas. Se analizó el efecto de diversos parámetros tales como temperatura, pH, concentración inicial de IC, entre otros.

**Palabras clave:** *Eichhornia crassipes*, indigo carmín, materiales nanoestructurados, óxido de manganeso.

Catalisador de MnO$_2$ nanoestruturado em *E. crassipes* (jacinto da água) para a degradação do índigo carmim

**Resumo**

Foi estudada a utilização de matéria seca do jacinto de água (*Eichhornia crassipes*) como matriz de suporte para nano-MnO$_2$ e sua aplicação para a remoção de indigo carmin (IC). Diferentes processos de pré-tratamento foram testados e os resultados indicaram que o pré-tratamento ácido-álcali é um método eficiente para ligar os NPs à matriz celulósica. Além disso, as NPs de MnO$_2$ foram sintetizadas por redução sonoquímica de MnO$_2$$_5$ utilizando diferentes métodos (um sistema emissor de ultrassom, banho de ultrassom e a reação com o etanol). O material sintetizado foi caracterizado por ATR-IR, AAS, DRX, SEM, isómeras de adsorção de nitrogênio, EDS e pH$_{\text{pzc}}$. A facilidade de remoção de IC por o material nanoestruturado e a natureza química da degradação dos produtos foram explorados em amostras aquosas, assim mesmo foi estudado o efeito de vários parâmetros (temperatura, pH, concentração inicial de IC e a quantidade de nanocompósito, entre outros).

**Palavras-Chave:** *Eichhornia crassipes*, indigo carmim, material nanoestruturado, óxido de manganeso.
**Introduction**

Nowadays, large amount of several synthetic dyes are used in textile, pharmaceutical, cosmetics, beverages, and electronic components industries. Around 10-15% of these dyes, employed by textile industry, are released into effluents, polluting both surface and ground water (1, 2).

Indigo (IN) or 2,2'-bis-indole, a blue synthetic dye, is one of the most consumed dyes in the industry, mainly employed for clothes dyeing. In order to enhance its solubility and improve the dyeing process, IN is often transformed into indigo carmine (IC) (indigo disulphonic 5-5’) (3, 4). However, in spite of its extensive use, IC has been linked to high toxicity (5).

The environmental and health concern of these potential pollutants in water has drawn attention of many researchers (6). In this regard, the application of metal oxide nanoparticles for treatment of contaminated effluents by dyes has become another challenging field in recent years. Manganese oxides, for instance, exhibit outstanding structural multif ormity as well as special magnetic and electrochemical properties. Therefore, manganese oxide catalysts show considerable activity in oxidation-reduction reactions (7-9).

Similarly, nanomaterials have wide applications as catalysts for dyes degradation (1, 7-11). The application of metal oxides in nano-size, however, has several engineering limitations that restrict its large-scale implementation. For example, these materials occasionally cause the leaching of nanoparticles (NPs), along with the treated effluent, resulting in even more serious environmental problems. Some of these limitations can be prevented by anchoring the nanoparticles on suitable matrices (9).

The water hyacinth (WH, *Eichhornia crassipes*), which is a widely prevalent aquatic weed in India, Australia, Africa, and South America, reproduces itself in five days under favorable conditions, obstructs oxygen transfer in water bodies and affects aquatic ecosystems. For this reason, it is considered one of worst invasive aquatic plants (12, 13). In spite of that, WH is an inexpensive, readily available biomass resource, which has been widely investigated for its high adsorption capacity (2, 14-16).

For the previous reasons, in this research, the use of dried matter of WH as a support matrix for MnO₂ NPs for removing IC from waste effluents was studied.

**Materials and methods**

**Materials**

Fresh WH plants were raised from stolons obtained from Muña Dam area in Colombia. The plants were placed in a clean water reservoir (4° 35’10’’N, 74°18’ 0’’W) at environmental conditions (day/night temperatures: 13-11°C/10-8°C). After the plant has reached an approximate length of 35 cm, the plants were extracted, washed several times, and dried at 80 °C for 24 h. Then, they were cut into small pieces (5 to 3 cm in length), and finally the plants were grounded with a ball mill.
Dye degradation experiments and catalyst reuse

The objective of the biomass pretreatment was the removal of lignin and hemicellulose, cellulose crystallinity decrease, and the material porosity improvement, so that MnO₂ NPs could effectively bind to the cellulose matrix. According to Table 1, the acid-alkali pretreated WH (PT2) exhibited the largest surface area (6.74 m²/g), which is six times the surface area showed by the WH biomass before any chemical modification. Although the surface area of WH biomass reported by others (1.80-4.50 m²/g) (14-16) clearly differs from the value found in this study (1.28 m²/g), this could be explained by the different growth conditions of the WH plants evaluated in each study.

Table 1. Surface area for pretreated WH

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WH</td>
<td>1.28</td>
</tr>
<tr>
<td>Pretreated WH (PT2)</td>
<td>6.74</td>
</tr>
<tr>
<td>Pretreated WH (PT3)</td>
<td>3.56</td>
</tr>
<tr>
<td>Pretreated WH (PT4)</td>
<td>5.44</td>
</tr>
<tr>
<td>Pretreated WH (PT5)</td>
<td>6.57</td>
</tr>
<tr>
<td>Comercial Activated Carbon</td>
<td>634.2</td>
</tr>
</tbody>
</table>
Lignin, hemicellulose, and cellulose content onto the WH biomass surface after the pretreatment, was evaluated by ATR-IR, and the results suggested, similarly to previous reported studies in other lignocellulosic materials (18-20), that the combined pretreatment method acid-alkali (PT2) is the best suitable method to obtain much better activated biomass surface (Figure 1). The normalized FT-IRs show that the acid-alkali pretreatment increases the –OH signal in comparison with the WH untreated, which suggest that more –OH groups are exposed, leading to a higher number of centers for NPs growth. This is further supported by the increase of the signals for C-O-C bonds (1008-1109 cm⁻¹), assigned in previous reports to an increase in the cellulose content on the material surface. In other words, PT2 has a lower lignin-hemicellulose and greater cellulose content than any other sample analyzed, including the WH untreated.

![Figure 1. ATR-IR spectra of the pretreated WH samples](image)

The positive results for the combined acid-alkali pretreatment can be explained because the H₂SO₄ pretreatment can effectively dissolve the hemicelluloses (xylan) and increase the enzymatic digestibility of cellulose, achieving high reaction rates in comparison with the enzymatic processes (21, 22). Furthermore, it is known that the main effects of NaOH pretreatment on lignocellulosic materials, such as the WH biomass are, firstly, the delignification by breaking the ester bonds cross-linking lignin and xylan, and secondly, the increase of the hemicellulose solubility (19, 23).

Due to this alkali pretreatment, a large number of hydroxyl groups (R-CH₂-OH), contained in the biological tissues, are converted in salts (R-CH₂-ONa) and incorporated into the biological templates. Because of the resulting high porosity and ionic environment, the MnO₄ accesses the hierarchical pore channels and forms MnO₂ NPs inside the pores more easily (19). Additionally, the NaOH causes the swelling of the biomass, which increases the internal surface area of the WH and decreases the cellulose crystallinity (24).

### NP synthesis

As mentioned above, for this study the NPs deposition was carried out by two principal methods: ethanol and ultrasonic assisted synthesis (sonochemical reaction). In both cases, the pretreated yellowish WH biomass (obtained after PT2) was immersed in the KMnO₄ precursor solution to replace Na⁺ for MnO₂⁺ ions into the R-CH₂-ONa centers formed during the pretreatment. Subsequently, the MnO₂⁺ ions over the WH surface were reduced either by the addition of ethanol or by the ultrasonic waves to finally deposit MnO₂ NPs onto the WH.

On the one hand, in the ethanol-assisted synthesis, the KMnO₄ present in the precursor solution acts as an oxidizing agent in neutral medium, water in this case. The ethanol is oxidized into acetic acid and permanganate is reduced, leading to the precipitation of MnO₂ and to the KOH formation (25). On the other hand, and regardless the ultrasonic waves generation method (bath or horn), the sonochemical reduction of MnO₂⁺ proceeds according to the following reaction [1], where the H₂ comes from the sonochemical dissociation (by radicals formation) in the aqueous solution.

\[
2\text{MnO}_4^{\text{(aq)}} + 3\text{H}_2\text{(g)} \rightarrow 2\text{OH}^-\text{(aq)} + 2\text{H}_2\text{O}\text{(l)}
\]

In other words, acoustic cavitation from ultrasonic synthesis produces reactive radicals, which exhibit extremely high cooling rates and can effectively reduce metal ions to metallic nanoparticles or metal oxide nanoparticles (19, 20).

In this study, the formation of MnO₂ was verified by UV-Vis at 530 and 320 nm for MnO₄ and MnO₂, respectively; and the pH values during the synthesis were verified too. In this regard, the pH increases from 7.3 to around 11.2 during the reactions, due to the production of OH⁻ ions ([1]). An abrupt change of color was observed after all synthetic methods, starting from the characteristic dark purple of aqueous permanganate to a yellowish color at the end of the reaction, similar to the observations reported in other studies (20).

### Characterization

As mentioned above, the AAS technic was used to quantify the Mn content deposited on WH, following the National Environment Protection Council procedure (17). The highest percentage of Mn on WH surface was found for sample 1 (33.3%, w/w), which could be explained by the longest contact time of the activated WH biomass with the KMnO₄ solution (100 mM, 3h). On the contrary, the ultrasonic syntheses (sample 2 and 3) were performed during 45 and 10 min and the percentages of Mn deposited on each of these surfaces were 21.7 and 28.8% (w/w), respectively (Table 2). The periods of time for each method were determined according to the equipment capacity and previous studies reporting successful MnO₂ NPs synthesis at the same conditions. According to the analysis by electron microscopy, the Mn particles deposited on the WH biomass have at least one dimension in the order of nanometers, it is possible to say that most of Mn was deposited as NPs.
Moreover the XRD patterns showed no further visible changes and no peak corresponding to MnO A even for the bionanocomposites MnO-A synthesized under different conditions. This might be attributed to the presence of very small crystals which are apparently below the detection limit of XRD or might be due to the amorphous nature of the MnO prepared. The EDX analysis of bionanocomposite MnO-A sample showed the characteristic signal for Mn at 5.92 eV. These XRD and EDX results coincide with previously reported studies of MnO NPs synthesized under similar experimental conditions.

The EDX spectrum also showed a signal of Pt around 5.9 eV which corresponds to the Pt coating used for the analysis.

The scanning electron micrographs of MnO-A sample exhibited a surface texture, porosity, and cavities of high irregularity in which the deposition of spherical agglomerated MnO NPs occurred. All these in agreement with previous reports of MnO NPs.

Although the percentages of Mn deposited on samples 2 and 3 were both lower in comparison with sample 1, the contact time for the NPs synthesis related with each method must be taken into consideration: sample 1 needed more than 4 times the contact time needed by sample 3 and approximately 21 times the contact time needed by sample 2, suggesting that the ultrasonic synthesis is more effective for the case of study.

The synthetized MnO-A catalyst, as well as the untreated and the acid-alkali pretreated WH (PT2), were analyzed by XRD in order to describe the crystallinity and structural properties before and after the MnO NPs formation. The XRD patterns showed in all cases a peak around 20=23° which has been attributed to the high intensity (002) plane of crystalline cellulose. At this 20, WH PT2 showed the most intense peak, confirming that the cellulose content increases as a consequence of the pretreatment, in comparison to the dried WH.


![Figure 3. SEM images of MnO-A-WH sample 1 at a) 30 µm, b) 1 µm, c) 300 nm.](image)

**Table 2. Mn content on WH by different NPs synthesis methods**

<table>
<thead>
<tr>
<th>Sample</th>
<th>MnO-NP-WH synthesis</th>
<th>Contact time (min)</th>
<th>Mn on WH (% w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO-NP-WH (Sample 1)</td>
<td>Ethanol assisted</td>
<td>180</td>
<td>33.32</td>
</tr>
<tr>
<td>MnO-NP-WH (Sample 2)</td>
<td>Ultrasonic-bath</td>
<td>45</td>
<td>28.74</td>
</tr>
<tr>
<td>MnO-NP-WH (Sample 3)</td>
<td>Ultrasonic horn</td>
<td>10</td>
<td>21.67</td>
</tr>
</tbody>
</table>

**Dye degradation experiments and MnO-A-WH catalyst reuse**

For each degradation test, the variation of the dye concentration was monitored measuring the UV-Vis absorbance at λ = 600 nm, using a pre-established calibration curve. The amount of dye absorbed (q) at any time t was calculated from equation [2].

\[
q_t = \frac{V(C_0 - C_t)}{W}
\]

[2]
Where, at equilibrium $q_e = q$ and $C_e = C$. And $q$, $C_i$, and $C_e$ are the initial, any time, and equilibrium concentrations of the dye solutions (mg/L), respectively. $V$ is the solution volume and $W$ is the mass of adsorbent (28). The dye removal percentage $[\text{Re}(%)]$ was calculated as follows:

$$\text{Re}(\%) = \left( \frac{C_i - C_e}{C_i} \right) \cdot 100$$

[3]

Prior to the degradation experiments, the catalyst was placed in a small sealed paper bag (similar to a tea bag) in order to prevent the MnO$_2$-NP-WH catalyst diffusion in the solution, facilitate the catalyst withdrawn process, and to slightly approach the experimental set up to an industrial design (Figure 4a).

![Figure 4. a) Paper bag with MnO$_2$-NP-WH inside b) Experimental set-up c) Color change of the solution before and after the contact with the MnO$_2$-NP-WH catalyst](image)

The first degradation tests were conducted at pH 7 using 1.0 g of MnO$_2$-NP-WH catalyst in a 20 ppm solution of IC. No change in the initial dye concentration was observed during these attempts even after 2 h of contact. However, pH variations (2.3, 4.5 and 7.0) in additional experiments showed that the best results for IC removal were obtained at pH = 2.3 (Figure 4b-c). The IC removal efficiency comparison between the MnO$_2$-NP-WH catalyst synthesized (sample 1, 2 and 3) and the WH samples (Figure 5), showed that all nanobiocomposites had much better IC degradation rate than the non-modified WH, pretreated WH, and also to the activated carbon, evaluated as absorbent solid. It must be noted that MnO$_2$-NP-WH sample 2 is the fastest IC degradation catalyst, requiring only 5 min to achieve the 97.6% dye removal. For the same degradation results, the activated carbon needed more than 50 min.

This removal effectiveness at lower pH conditions is favored by the presence of -SO$_3^-$ groups over the IC structure (27). As a consequence, at acidic conditions, the MnO$_2$-NP-WH bionanocomposite surface is protonated, increasing the electrostatic interactions with the IC molecules as well as the degradation rate.

![Figure 5. Dye removal at 22°C and pH = 2.3. Insert: UV-Vis monitoring of IC color removal](image)

To support the above hypothesis, the pH$_{pzc}$ of the biocomposite was determined. The point of zero charge (pzc) describes the condition when the electrical charge on a surface is zero and it is frequently determined in relation to an electrolyte’s pH. In other words, pH$_{pzc}$ is usually the pH value at which a solid submerged in an electrolyte exhibits zero net electrical charge on the surface (29). Therefore, in NP synthesis, cations adsorption is favored at pH > pH$_{pzc}$, while the anions adsorption is favored at pH < pH$_{pzc}$ (30). For the WH biomass a value of pH$_{pzc}$ = 4.5 was obtained, which means that WH surface is positive charged at pH < 4.5. Then, there is a strong electrostatic interaction between the WH surface and the IC molecules at low pHs, promoting the dye adsorption and degradation. Similarly, other studies reveal the high dependence of the MnO$_2$ surface on the pH solution, in those a pH pzc value between 4-5 was determined as optimal (20, 31).

The temperature effect on IC degradation was tested for MnO$_2$-NP-WH sample 2 at pH = 2.3. The results show that the bionanocomposite performs better at low temperatures (Figure 6), which is a positive variable in the case of scaling up experiments. The physicochemical explanation and implications of these results are under studying at moment by this group.

![Figure 6. IC removal in time by varying temperature at pH = 2.3 for sample 2](image)
To measure the reuse capacity of the MnO$_2$-NP-WH catalysts, sachets with 0.5 g of bionanocomposite were sequentially placed into seven different IC fresh prepared solutions; the characteristic absorption in each solution was followed by UV-Vis after 5 min contact (Figure 7). The results showed that the degradation capacity for the untreated WH was just 30% of the initial after seven cycles of usage. Meanwhile, by comparing the last cycle with the initial for MnO$_2$-NP-WH samples 1 and 3, the degradation capacity was lightly reduced in just 5 and 3%, respectively. Interestingly, the dye removal of MnO$_2$-NP-WH sample 2 decreased abruptly after the sixth cycle of usage. The possible reasons for these variations in reuse capacity are: (i) occupation of available adsorption sites within the WH matrix by IC molecules and (ii) leaching of MnO$_2$ NPs to the solution, reducing the number of active reaction sites on the bionanocomposite surface.

In order to characterize the IC degradation products, the solution, before and after IC color removal process, was monitored by ESI-MS in negative ion mode. Similar to what was reported by Combariza et al. (20), the ESI-MS for the initial IC solution presented a unique and characteristic base peak at m/z 421, corresponding to IC in its anionic form (32). After 5 min of degradation, there was no signal for IC; instead, several peaks were shown at m/z 190, 226, 237, 253 and 257.9 (Figure 8). Among these signals, the peak at m/z 226 has been previously assigned to the oxidative breaking of the initial C-C bond and it have been identified as isatin sulfonic acid (20, 32-34).

![Figure 7. IC removal (T = 22°C, pH = 2.3) after consecutive reuse cycles. a) WH untreated; b) MnO$_2$-NP-WH sample 1; c) MnO$_2$-NP-WH sample 2; d) MnO$_2$-NP-WH sample 3](image1)

![Figure 8. a) ESI-MS after a reaction time of 5 min; b) Indigo carmine (m/z 421) and isatin sulfonic acid (m/z 226), one of the few degradation products identified](image2)
Conclusions

The water hyacinth (Eichhornia crassipes) has a great potential as solid matrix for the deposition of MnO₂ NPs and as catalyst in the organic dyes degradation, due to its surface morphology and high adsorbent capacity. It is therefore an economic and practical alternative for the solution of two current environmental issues: (i) water contamination, due to the extensive withdrawal of toxic dyes such as IC, and (ii) the invasion of water reservoirs caused by the WH extremely fast proliferation and growth, which presents serious environmental, economic, and navigation challenges, among others.

The NPs synthetic methods studied in this investigation, ethanol and ultrasonic-assisted, both provided suitable conditions for the deposition of MnO₂ NPs over cellulose matrices under the described experimental parameters. It was found that the ethanol-assisted synthesis produces the highest deposition of manganese onto the pretreated WH (33.3%) in comparison with the ultrasonic bath (28.7%) and horn-assisted (21.7%) synthesis. However, the leaching of MnO₂ particles is considerable lower after the ultrasonic synthesis and the catalyst reuse produces therefore better results by this synthetic methodology.

The results showed that the MnO₂-NP-WH bionanocomposites constitute effective catalysts for the IC degradation in aqueous solution at 23 °C, pH = 2.3 and 5 min contact time. Under these conditions, 97.6% of IC can be degraded (percentage as function of decrease in absorbance at the xmax for IC). Finally, the mass spectrometry analysis evidenced that although some pure absorption processes by the WH matrix cannot be ruled out, a chemical degradation of the dye was confirmed.

References


**Article citation:**