Removal of dye from wastewater by titanomagnetite nanoparticles loaded yeast biomass hierarchical composite

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ABSTRACT: This study focused on the synthesis and application of new magnetic nanoparticle based adsorbent for the removal of dye from wastewater. Titanomagnetite nanoparticles were synthesized and impregnated on yeast biomass (YB) a byproduct generated from the ethanol industry, producing a composite (T-YB). Both materials are characterized using X-ray diffraction, FTIR, BET and UV-Vis spectrophotometer. The as prepared adsorbents were tested for adsorptive removal of dye, exemplified by methylene blue, from wastewater using the batch adsorption mode. The adsorption equilibrium data, for both materials, yeast biomass with and without titanomagnetite nanoparticles, were analyzed using the SIPS model. Higher adsorption capacity was obtained upon incorporating nanoparticles with yeast biomass, increasing the dye recovery in 20.3% and denoting a higher affinity to the adsorbate. In addition, the magnetic proprieties of T-YB make it possible to be recovered from the aqueous medium using a magnet, thus eliminating the centrifugation or filtration steps.

KEYWORDS: nanocomposite; titanomagnetite nanoparticles; methylene blue; yeast biomass.

1. INTRODUCTION

The presence of high concentration of colors and dyestuff in water bodies blocks the light in aquatic bodies, impairing the photosynthesis affecting all marine and lentic environmental animals (Mor et al., 2017). Different water treatment processes can be used to remove dyes and colors from water, such as photodegradation, advanced oxidative processes and membrane filtration. However, these processes suffer from some challenges as they are expensive to be implemented and ineffective in meeting stringent environmental standards (Chienget al., 2014). The sorption process can be considered an alternative due to its simplicity and cost-effectiveness, once it usually employs residues and agricultural wastes (De Gisi et al., 2016).

The yeast biomass employed in this study, is a residue from the fermentation processes in the ethanol industry. This material presents functional groups that can be able to act as sorption sites (Labuto et al., 2015).

Associating materials that are usually used in sorption processes with magnetic nanoparticles has been shown to be viable and advantageous, once it is possible to eliminate the centrifugation or filtration steps, which are replaced by removing the material from the solution through a magnetic field. The use of magnetic materials for environmental applications has been increasing due to their potential to support and complement other treatment processes (Madarakian et al., 2012; Tan et al., 2012; Raj & Joy, 2015; Song et al., 2015).

The titanomagnetite nanoparticles present magnetic properties and present the
advantage that to be a natural material being environmentally friendly (Liu et al., 2013; Wilie et al., 2016).

This study described the synthesis and application of a new nanoparticle based adsorbent for removal of dye, exemplified by methylene blue, from wastewater using the batch mode adsorption process. Herein, we prepared titanomagnetite nanoparticles loaded yeast biomass materials (T-YB) and employed it for the first time for cleaning up wastewater from dyestuff.

2. MATERIALS AND METHODS

2.1. Synthesis of nanocomposite
Iron (II) sulfate heptahydrate, titanium tetrachloride, ammonium hydroxide and hydrogen peroxide (30%) were purchased from Sigma-Aldrich. Solid yeast biomass residue was collected from an ethanol industry (São Paulo State, Brazil). The titanomagnetite nanoparticles were synthesized by dissolving iron (II) sulfate heptahydrate into the water, followed by addition of titanium tetrachloride and ammonium hydroxide, that was stirred for 2 min. At this moment, hydrogen peroxide solution (30%) was added to the mixture, which was stirred for 20 min. The titanomagnetite nanoparticles were produced and then incorporated within the yeast biomass residue (83% m/m), by agitating them into the reaction medium for 30 min, resulting in a new hierarchical material called T-YB. The material was washed with water several times during vacuum filtration and then dried in desiccator. All procedures were performed at room temperature. The dried material was characterized and used in methylene blue adsorption studies.

2.2. Material characterization
The crystal structure of the as prepared materials was determined by powder X-ray diffraction (XRD) analysis using a Rigaku ULTIMA III X-ray diffractometer with Cu Kα radiation. The scans were done in the 2-theta range of 3–90, using a 0.05-degree step and a counting time of 2.0 degrees per min. The equipment operated at 40 kV and 44 mA.

2.3. Methylene blue adsorption studies
Methylene blue chloride (82%) was purchased from Sigma-Aldrich and used as adsorbate in the adsorption studies. Different concentrations of methylene blue solution were prepared, and around 50 mg of adsorbent were exposed to the different concentrations in 10 mL volume of the methylene blue solution, followed by shaking for 2 h. For these studies, two adsorbents were tested, the yeast biomass residue from ethanol industry and the titanomagnetite nanoparticles loaded yeast biomass materials (T-YB). The adsorbent was separated from the solution by centrifugation at 10,000 rpm for 10 min. using an Eppendorf Centrifuge 5804. The supernatant was measured by UV-Vis Spectrophotometry (Nicolet Evolution 260 Bio, Thermo Scientific) at a wavelength of 665 nm, in which has the maximum absorbance for methylene blue, to determine the remaining concentration of methylene blue. The solid was recovered, dried at room temperature and analyzed by Fourier Transform Infrared (FTIR). FTIR spectra were obtained using the IRAffinity-1S, Shimadzu. Each sample was scanned 50 times with 4 cm⁻¹ resolution, in the range of 400 cm⁻¹ - 4000 cm⁻¹. All the experiments were carried by triplicate at room temperature.

3. RESULTS AND DISCUSSION

3.1. Material characterization
Figure 1 shows the XRD patterns of the YB and T-YB samples, where each signal represents plane reflections from the crystalline structure. The diffractogram was compared with a database using the software JADE V.7.5.1 (Materials Data XRD Pattern Processing Identification & Quantification), that confirmed the titanomagnetite structure (#01-071-6450 pdf card). The yeast biomass
residue presents an amorphous structure; thus no crystalline order is observed on the diffractogram. In addition, the yeast biomass did not affect the titanomagnetite crystallinity upon combination.

Figure 1. Diffractograms of A) T-YB; B) YB.

3.2. Methylene blue adsorption studies
Using UV-Vis spectrophotometry the remaining concentration of methylene blue was established. Afterwards, the experimental data for methylene blue adsorption onto YB and T-YB were plotted. Furthermore, this data was described by SIPS model using Origin 8.0®, as can be seen in Figure 2. The fitting parameters obtained for SIPS model for both materials are shown in Table 1.

As seen in Table 1, the R² is nearly 1.0 for both adsorbents, thus SIPS isotherm best fit the experimental data. Moreover, the Q_m presents a value close to the sorption capacity, which was 47.1 for the YB and 53.0 for the T-YB samples, corroborating the SIPS best fitting. In addition, the T-YB presents a higher K_s value than the YB, indicating a higher affinity for methylene blue than the yeast biomass. This observation denotes that the T-YB improved the recovery of methylene blue from water with an increment of 20% in the adsorption capacity. Furthermore, the magnetic characteristic of T-YB favors the adsorbent recovery from the aqueous solution after the completion of the adsorption process.

Table 1. Values of the constants for the best fitting for methylene blue adsorption onto the adsorbents following SIPS isotherm.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Yeast Biomass</th>
<th>Nanocomposite</th>
</tr>
</thead>
<tbody>
<tr>
<td>K_s (L mg⁻¹)</td>
<td>0.0181</td>
<td>0.419</td>
</tr>
<tr>
<td>n_s</td>
<td>1.24</td>
<td>0.509</td>
</tr>
<tr>
<td>Q_m (mg g⁻¹)</td>
<td>48.3</td>
<td>58.1</td>
</tr>
<tr>
<td>R²</td>
<td>0.997</td>
<td>0.985</td>
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</table>
As SIPS is a combination of Langmuir and Freundlich models, the heterogeneity factor ($n_s$), can denote whether the model resembles more to Langmuir or Freundlich. The SIPS model can be reduced to Langmuir if $n_s$ is equal to 1, and to Freundlich when $n_s$ is equal to 0 (Belhachemi & Addoun, 2011; Alves et al., 2016; Podder & Majumder, 2016). For the YB, $n_s$ is 1.24, meaning that it follows Langmuir, however, lateral interactions can occur between the adsorbate molecules (Hmoudah et al., 2016). Whereas the T-YB shows $n_s = 0.509$, corresponding to an intermediate value ($0 < n_s < 1$), thus a true combination of Langmuir and Freundlich models.

The FTIR was performed to confirm the methylene blue adsorption by YB and T-YB (Figure 3).

![Figure 3. FTIR spectra of Methylene blue (MB), and YB and T-YB after MB adsorption.](image)

The methylene blue shows characteristic bands in 578, 1051, 1396, 1450, 1558 cm$^{-1}$, corresponding, respectively, to C-S-C vibration, C-S bond, C-C bond, -CH$_3$ groups and aromatic ring stretch (Song et al., 2015). The main changes in the YB and T-YB spectra were in 1290, 1564, 2330 and 2370 cm$^{-1}$ denoting the methylene blue adsorption.

### 4. CONCLUSIONS

Titanomagnetite nanoparticles were successfully synthesized and incorporated onto the surface and cavities of the yeast biomass (T-YB) generating in this way a novel hierarchical composite material. T-YB was employed for removal of methylene blue, which showed a 20% improvement in the adsorption capacity in comparison with virgin yeast biomass. The adsorption isotherms fit well to the SIPS model. The T-YB could be removed from solution by a simple magnet, making the adsorption process simpler and faster.

### 5. REFERENCES


6. ACKNOWLEDGEMENTS

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