
# GRAPHENE OXIDE-$Cu^{2+}$ INTERACTION EVALUATION USING THE COMBINATION OF MATHEMATICAL MODELS AND MOLECULAR FLUORESCENCE SPECTROSCOPY

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In recent years, the contamination of water by heavy metals such as copper has been the subject of many studies due to the high mobilization of this metal into freshwater through soils and residues from human activities such as mining, industry, and agriculture, consequently raising the concentration of a metal ion in the environment. Thus, it is essential to develop efficient methods, techniques, and materials for applications in treatments, remediation, sensing, and detection of pollutants. Carbon nanomaterials have gradually gained the spotlight, especially materials based on graphene, such as graphene oxide (GO), which has unique properties and presents interesting functional groups for environmental applications. Based on this, the present study evaluated the ability of graphene oxide to bind through chemical complexation to copper metal to understand and identify the mechanisms involved in these interactions. The analytical technique of molecular fluorescence was associated with Ryan and Weber's mathematical models and Stern-Volmer. Initially, synthesized GO was characterized by different techniques. Atomic force microscopy (AFM) topographical image showed few layers of stacked graphene and lateral sheet size of up to 2 square micrometers in area. The Fourier Transform Infrared Spectroscopy (FTIR) technique was essential and proved that the graphite was oxidized since there was the appearance of characteristic GO bands that correspond to the hydroxyl, carbonyl, carboxyl, and epoxy groups. The concentration of carboxylic groups found by potentiometric titration was 1.83 mmol of -COOH per GO gram. With Raman spectroscopy, it was possible to observe characteristic bands of carbon materials, one at ~1355 $cm^{-1}$, called the D band, associated with vibrational modes resulting from the structural disorder due to defects, functionalizations, and $sp^3$ carbons, and another band at ~ 1606 $cm^{-1}$ called the G band, characteristic of the vibrational modes of the carbon ring in the graphene sheet, and also the presence of second-order bands, located in the region between 2700 and 3200 $cm^{-1}$. Finally, UV-Visible spectroscopy highlighted the typical GO spectra that present two characteristic bands, one at 300 nm attributed to the $n \rightarrow \pi^*$ transition of the C=O bond and the other at 228 nm associated with the $\pi \rightarrow \pi^*$ transition of the C-C bonding of aromatics. As a result, the GO showed fluorescence in the visible region, with maximum intensity for $\lambda exc$=520 nm and $\lambda em$=450 nm. The suppression of the fluorescence signal was monitored by titrating the GO solution with increasing concentrations of $Cu^{2+}$, and it was possible to notice a gradual attenuation in the intensity values according to the increase in copper concentrations, a result of the interaction of copper with conjugated and aromatic structures, as well as groups containing oxygen. The mathematical modeling that best fitted the intensities was that of Ryan and Weber, due to the non-linear adjustment. This same model showed an excellent interaction of GO with the metallic ion, due to the values of Log K = 3.19 and CL of $5.93 \times 10^{-5}$ mol $L^{-1}$, which are very similar for different species found in organic matter natural such as humic and fulvic acids, which have a chemical structure close to the GO structure. These values indicate that GO has similar behavior to these molecules in copper complexation. An important factor is a growing search for materials for environmental remediation that mimic natural molecules. Another relevant aspect was that from intensity 38.1 onwards, the fluorescence did not decrease further, proving the ability of copper to complex with the binding sites available for graphene oxide interaction. Thus, GO can have an efficient approach to interact with metals and can be a new tool for remediation and control of areas contaminated by copper ions, such as acting as a sensor for detecting high concentrations of the metal ion.

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