Modified graphene oxide/chitosan composites for the adsorption of Methylene blue and Reactive black 5 from dyeing mixtures

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Water pollution has been significantly increased the last decades, mainly because of the huge amount of insufficiently treated wastewater disposed in it (Amin 2014; Yan et al. 2016; Yuan, Meng, and Park 2016). As a result, the design and development of advanced wastewater treatment plants have a strong appeal and as an extension, it has become important to develop new composite materials that are sustainable and environmentally friendly. Conventional wastewater treatment methods include a wide range of techniques that fall into the broader categories of physical, chemical or biological methods and are performed individually or in combination, in order to achieve the highest possible purification of the effluent. In terms of water pollutants, dyes are one of the main categories found in wastewaters. That is because dyes are the products of many different industries, such as pharmaceutical, cosmetics, leather, printing and textiles. In fact, it has been found that over that 100,000 types of dyes are currently manufactured, and as a result, a great percentage of them end up in water resources (Nilay Kahya 2021). With that been said, and considering the fact that most dyes have toxic outcome for the aquatic environment and all the living beings, the interest of the global scientific community for efficient wastewater treatment grows rapidly and remains an ongoing challenge.

Among the wide variety of techniques that have been used and studied for the decolorization of contaminated water streams, the most prevalent is undoubtedly adsorption (Nilay Kahya 2021; Ramesha et al. 2011). Adsorption is a surface phenomenon, defined as the retention of molecules, atoms or ions of various substances in the liquid or gas phase or dissolved solids, on the surfaces mainly of solids and rarely of liquids (Ouaddari 2024). Adsorption is probably the most efficient wastewater treatment approach as regards to dyes, because of its low operation cost and the fact that is overall a harmless process, with non-toxic by-products. Another great advantage is that the adsorbent can be reused multiple times without losing significantly its adsorption capacity (Massoud Kaykhaii 2018; Rahmatpour, Alijani, and Alizadeh 2023). Moreover, the adsorption method can be used for the removal of organic dyes, which are harmful for aquatic biota, human beings and are associated with carcinogenesis (Liu et al. 2023).

Regarding the adsorbents that are used, there has been progress in developing composites with non toxic polymers, like chitosan, to decrease the risk of these techniques. Chitosan (poly-β-(1→4)-2-amino-2-deoxy-D-glucose) is a polysaccharide, that is produced by N-deacetylation of chitin. Chitosan can be described as a non-toxic biopolymer, that presents hydrophilicity, high biocompatibility and biodegradability, and also high cost-effectiveness (G. Z. Kyzas 2018). Its chemical properties could be attributed to the functional groups appeared on its structure, such as hydroxyls (−OH), oxygen groups (−O−) and amines ($-NH_2$) (Yuan, 2016). However, chitosan has some disadvantages associated with its reusability, because at low pH levels, it has been found that chitosan decomposites rapidly (Trikkaliotis 2022). An effective approach to this issue, is the combination of chitosan with other polymers or/and nanomaterials, and thus its properties are significantly improved.

In the current work, chitosan is combined with graphene oxide, in order to produce an adsorbent for the enhanced removal of dyes from aqueous solutions. Graphene oxide is a derivative of graphene, used in a wide range of innovative applications, due to its unique physical and chemical properties. In detail, graphene can be described as a single layer of carbon atoms, and has honeycomb-like structure. Graphene oxide results from the oxidation of graphene, and on its surface has a plethora of functional groups such as hydroxyls, epoxides, carbonyls and carboxyls. These groups give the opportunity to graphene oxide to create strong bonds with a variety of polymers, like chitosan, and produce a material that is thermodynamically and chemically stable (Daniel J. Johnson 2021; Gkika 2023, Ramesha et. al. 2011). That structure modification is a critical for the adsorption capacity of the composite, and can lead to higher dye removal percentages, without having to provide any more energy to the system.

In the current study, a chitosan/ graphene oxide composite material is used as an adsorbent for the removal of one cationic and one reactive dye, Methylene Blue (MB) and Reactive Black 5 (RB5) respectively. The synthesis of the adsorbent was followed by batch adsorption experiments, where the effect of pH, contact time, initial concentration, temperature and initial mass of adsorbent were tested. The novelty of this experimental process is that the adsorption of the two dyes by Cs/GO composite happens at the same time. For the characterization of the produced adsorbents Fourier Transform Infrared spectroscopy (FTIR), X-ray diffraction (XRD), Scanning electron microscopy (SEM) and BET analysis were utilized, before and after adsorption. Pseudo-first and pseudo-second order equations applied in order to study the adsorption kinetic mechanism of MB and RB5 onto Cs/GO composite. The distribution of the adsorbent between liquid and solid interface was determined by fitting with Freundlich and Langmuir isotherm models. The overall results obtained revealed that the produced composite can provide a promising approach for the eco-friendly and low cost treatment in mixtures of model pollutants in aqueous solutions and ultimately in real wastewater.

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