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Development of a chitin/graphene oxide hybrid composite for the removal of pollutant dyes: Adsorption and desorption study

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HIGHLIGHTS

- The components' availability make this material a promising low-cost biosorbent.
- Oxidized groups in the nGO structure increase the reactivity of the hybrid.
- A hybrid composition endows it with adsorption versatility for acid and basic dyes.
- A high desorption degree could be achieve increasing the solution pH.
- Two powder components can be converged in a solid-like gel for adsorption processes.

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ABSTRACT

This work presents the synthesis of chitin (Chi) and chitin/graphene oxide (Chi:nGO) hybrid gels in mild conditions and their use as biosorbents in solid–liquid batch systems. The graphene oxide nanosheets, obtained from natural graphite through Hummers method, were characterized using FT-IR, ESR and pH_{pzc} determination as a qualitative approach of the degree of exfoliation and oxidation. Two kinds of widely used dyes were tested: Remazol Black (RB) as an acid dye model and Neutral Red (NR) as a basic dye model. Adsorption assays results were analyzed using two and three parameters isotherm models. The maximum adsorption capacity (q_m) for RB and NR were 9.3×10^{-2} mmol/g and 57×10^{-2} mmol/g being the first one reached by Chi and the second by the hybrid. Furthermore, the adsorption behavior over the time was evaluated through pseudo-first, pseudo-second, Elovich and Modified Freundlich models being the first one which described better all the cases except the adsorption of Remazol Black on chitin gel which follows an Elovich tendency. According to the pseudo-first order model, the uptake rates (k_1) were between 1.1×10^{-2} min^{-1} and 1.4×10^{-2} min^{-1}, but for the Chi:nGO-NR system it was 1.7×10^{-3} min^{-1}. The adsorption was observed to be dependent on both the solution pH and the Chi:nGO proportion. Finally, both dyes can be desorbed from both kinds of materials up to 60% of the sorbed amount by increasing the solution pH above 8. This would imply the capability of reutilization of the material with minor sorption capacity.

1. Introduction

Synthetics dyes have been widely used in textile, food, cosmetics, pharmaceutical industries and with microbiological purposes as well. With the development of technology and industry, more and more attention has been paid to dyes as water pollutants. The total dye production exceeds the 700,000 tons per year and about 2% of this production is discharged in effluent from manufacturing operations [1]. There are commonly about 10–15% of unused dyestuff entering the wastewater directly in the staining process but the loss of some reactive dyes in the dyeing process could reach 50% [2]. One of the major problems that water coloration entails is the reduction of sunlight transmission which affects photosynthesis and harms aquatic ecosystems [3]. In addition, many of the synthetic dyes are toxic and carcinogenic [4].

In the last years several wastewater treatment methods have been developed. Some examples of those techniques are coagulation, chemical oxidations and biological or enzymatic treatment.

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However, most of them are not capable of achieving high quality treated water or carry high implementation costs [5]. Depending on the adsorbent source, adsorption technologies represent one of the most efficient and cheap alternatives towards the treatment of wastewater which may contain several kinds of pollutants, for instance dyes. Other advantages of these decontamination methods are the facile scaling-up, high efficiency sorption without releasing any co-product to the environment and the possibility of recovering the adsorbent once the treatment is finished in the case of liquid–solid adsorptions [6].

Several adsorbent materials have already shown the potential for dye adsorption [6–8]. Chitin and chitosan, by-products of alimentary industry, are considered low cost biosorbents and have been studied for the removal of dyes from aqueous media [9,10]. Chitin is the second most abundant biopolymer found in nature after cellulose and can be found in fungi, the exoskeleton of insects and the shells of crustaceans, including shrimp and crab, as well as other invertebrates, such as marine sponges [11,12]. Its structure consists predominantly of unbranched chains of β-(1 → 4)-2-acetoamido-2-deoxy-d-glucose.

Carbon, especially activated charcoal, has also been widely used in water purification processes due to its high porosity and specific surface. Currently, other carbon allotropes, such as graphene, carbon nanotubes and fullerene have acquired an important role in the development of new nanostructured materials with several applications in the water remediation field. Graphene, in particular, is a one-atom thick layer of graphite where the carbon atoms are distributed in a regular sp^2-bonded network [13]. One of the most important features of graphene to be taken into account for its potential use in wastewater treatment, and other adsorption processes, is its great specific surface (2630 m^2/g) and flat geometry [14]. These characteristics would allow the production of lightweight materials with high adsorption capacity using low amounts of graphene [15]. However, the poor solubility of graphene nanosheets, due to the lack of polar groups in its molecular structure, could represent a drawback when the adsorption of polar molecules is pursued. In order to avoid this disadvantage, a facile method for increasing the hydrophilicity and reactivity of graphene is the synthesis of graphene oxide (GO) nanosheets through oxidative exfoliation from cheap graphite [16]. Finally, several researchers have reported the use of GO as a filler for polysaccharide based materials, such as starch, alginate, agarose, cellulose and chitosan, mainly aiming for the reinforcement of mechanical properties [17–22].

In a previous work, we presented a novel hybrid material composed by chitin and graphene oxide nanosheets [23]. The importance of the addition of GO to the chitin matrix relies not only in the proven composite reinforcement but also in a potential improvement of the adsorption versatility due to the dissimilar chemical nature of both components. The obtaining of a solid-like gel from two powders make the hybrid a promising alternative for wastewater treatment in heterogeneous phase (batch or continuous systems) [9].

The aim of the present work was to evaluate the adsorption capabilities of chitin/graphene oxide hydrogels in liquid media against two different pollutant dyes: Remazol Black (RB) and Neutral Red (NR). The first was considered as a model of acidic dye due to the presence of sulfonic groups in its structure. On the other hand, the NR acts as a cationic or basic dye because of the highly protonable amines in its structure.

2. Experimental

2.1. Reagents and materials

Natural graphite powder (<125 mm particle size) was purchased from Bitter (UK). Chitin from crab shells (DA: 92%; Mr ≈400,000) was obtained from Fluka (USA). Calcium chloride dihydrate and methanol were purchased from Anedra (Argentina) and Sintorgan (Argentina), respectively. Dyes Remazol Black and Neutral Red were obtained from Sigma–Aldrich (USA) and Riedel-de Haën (Germany), respectively. All other reagents were of analytical grade.

2.2. Preparation of graphene oxide nanosheets

GO nanosheets were prepared through Hummers method as described elsewhere [24]. The resulting graphite oxide was exfoliated into GO monolayer nanosheets (nGO) by sonication at 35 kHz for 30 min after dispersion in citrate buffer (0.4 M; pH: 4.2). Then the suspension was centrifuged and the pellet was washed with water and then with methanol. The methanol was removed by heating in a stove at 60 °C and the graphene oxide powder was then stored at room temperature.

2.3. Preparation of chitin hydrogel and chitin/nGO hybrid materials

To prepare a transparent calcium solvent, 42.5 g of calcium chloride dihydrate was suspended in 50 mL of methanol and refluxed for 30 min at 82 °C to a state of near-dissolution. One gram of chitin powder was suspended in the calcium solvent and refluxed for 2 h at 90 °C with stirring [25].

Different mass ratios of chitin and nGO were mixed by thorough agitation in order to obtain four types of hybrid materials with different chitin to graphene oxide ratios (Chi:nGO): 3:1, 1.2:1, and 0.6:1. For example, 10 g of chitin suspension, containing 120 mg of pure chitin, was mixed with 40 mg of nGO in order to obtain a hybrid material with a Chi:nGO ratio of 3:1.

The chitin/nGO mixtures were poured between two glasses spaced by glass slides of known width and then submerged in methanol until they gelled. Finally, the gels were subjected to several water incubations in order to wash out all of the methanol and $CaCl_2$ residues. Blank chitin gels without nGO were obtained by a similar procedure and named Chi. All the gels were cut in a circular geometry with 5 mm diameter x 2 mm width for all the experiments.

2.4. Material characterization

In order to determine qualitatively the degree of exfoliation and oxidation of the nGO, it was analyzed by Fourier Transform Infrared Spectroscopy (FT-IR), Electron Spin Resonance (ESR) and the drift method. The graphite and nGO powders were placed in a capillary tube and ESR spectra were recorded at 20 °C in an X-band ESR Spectrometer Bruker EMX plus (Bruker Instruments, Inc., Berlin, Germany). The spectrometer settings included: sweep width 150.00 G; center field 3515 G; microwave power 10.0 mW and conversion time 5.12 ms. For g factor calculation, Diphenylpicrylhydrazyl (DPPH, Aldrich) (g = 2.0036) was used as an internal standard. FT-IR transmission spectra were acquired in the range 4000–400 cm^{-1} using a FTIR Spectrometer (Nicolet 360). All samples were previously dried for 24 h at 60 °C to avoid water related band interference. Scanning Electron Microscopy (SEM) images of freeze-dried and gold coated samples were taken using a FEI Quanta 200 microscope. The pH of the point of zero charge (pH_{pzc}) of nGO was determined by the drift method, where the pH point at which the curve of the final pH crosses the $pH_{initial} = pH_{final}$ line is the pH_{pzc} [26].

2.5. Adsorption experiments

Adsorption experiments were carried out by a batch method in a room with controlled temperature (25 °C) and constant stirring