



Benzene carboxylic acid derivatized graphene oxide nanosheets on natural zeolites as effective adsorbents for cationic dye removal

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HIGHLIGHTS

- Natural zeolites were modified with graphene oxide (GO) via a condensation reaction.
- The GO was then modified using a diazonium salt to produce carboxy-GO/zeolite powder.
- The kinetics of rhodamine B adsorption onto the carboxy-GO/zeolite was very fast.

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ABSTRACT

Graphene oxide (GO) nanosheets were grafted to acid-treated natural clinoptilolite-rich zeolite powders followed by a coupling reaction with a diazonium salt (4-carboxybenzenediazoniumtetrafluoroborate) to the GO surface. Raman spectroscopy, Fourier transform infrared (FTIR) spectroscopy, and thermogravimetric analysis (TGA) revealed successful grafting of GO nanosheets onto the zeolite surface. The application of the adsorbents for the adsorption of rhodamine B from aqueous solutions was then demonstrated. After reaching adsorption equilibrium the maximum adsorption capacities were shown to be 50.25, 55.56 and 67.56 mg g⁻¹ for pristine natural zeolite, GO grafted zeolite (GO-zeolite) and benzene carboxylic acid derivatized GO-zeolite powders, respectively. The adsorption behavior was fitted to a Langmuir isotherm and shown to follow a pseudo-second-order reaction model. Further, a relationship between surface functional groups, pH and adsorption efficiency was established. Results indicate that benzene carboxylic acid derivatized GO-zeolite powders are environmentally favorable adsorbents for the removal of cationic dyes from aqueous solutions.

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1. Introduction

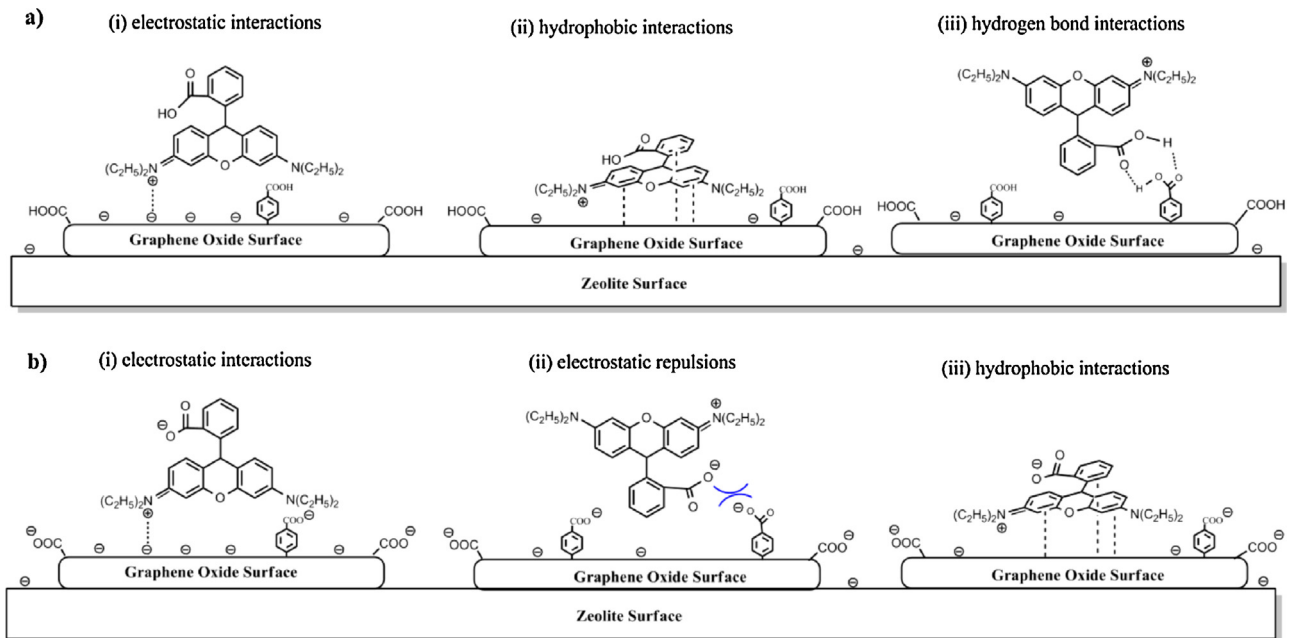
Dye effluents generated from textile printing and dye manufacturing often exhibit toxic effects on aquatic environments [1]. In order to remove these dyes, and other contaminants, physical, chemical and biological methods such as adsorption [2], coagulation [3], chemical oxidation [4], photodegradation [5], and aerobic or anaerobic treatment have been developed [6]. By far the most simple, efficient, cost-effective and versatile method amongst adsorption technologies is the use of solid porous materials, for example, activated carbon [7], aerogels [8], zeolites [2], clays [9] and kaolinite [10]. In particular, activated carbon is widely used for the removal of effluent dyes due to its high surface area, porous structure, and high adsorption efficiency and capacity

[11,12]. However, there is a high energy cost to production and issues associated with regeneration. Therefore, there has been an increasing focus on utilizing low-cost environmentally friendly materials for environmental remediation.

One material in particular, natural zeolites, affords a cheap option to effluent clean-up. Natural zeolites are microporous aluminosilicate crystalline minerals with 3-dimensional frameworks of tetrahedrally coordinated SiO₄ or AlO₄ [13]. Various cations (e.g., Na⁺, K⁺, Ca²⁺, and Mg²⁺) are loosely held in the zeolite pores, channels or cavities which can be exchanged with other organic compounds (e.g., dyes, humic acids or phenolic compounds) and inorganic cations (e.g., Hg²⁺, Pb²⁺, Ag⁺, Cu²⁺, Cd²⁺, Cr²⁺, Co²⁺ or Mn²⁺) [14–19]. The use of natural/modified zeolites for environmental remediation and wastewater treatment applications has been gaining significant interest due to their microporosity, moderate/high surface area, ion-exchange properties, low cost and worldwide occurrence [20,21]. Recent studies have shown that natural zeolites have a good affinity for basic dyes in aqueous solution

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Scheme 1. Three possible interactions between carboxy-GO/zeolite sample and rhodamine B at (a) pH = 3 and (b) pH = 5.

(e.g., methylene blue [2,22], reactive red 195 [23], reactive blue 21 [23] and rhodamine B [22,24]).

Potentially, the dye adsorption performance of natural zeolites could be enhanced by surface modification and/or functionalization. A good candidate for this is graphene oxide (GO), a single layer nanosheet of oxygenated graphene sheets [25]. The oxygen functionalities in GO include epoxy and hydroxyl groups, which lie on the basal planes of the GO sheets while carboxyl groups are mostly found at the GO edges [25]. These oxygen containing functional groups make the GO nanosheets negatively charged and hydrophilic. Moreover, GO has a strong propensity to interact with positively charged species such as metal ions [26], dyes [27–29] and biomolecules [30].

Further modification of GO can be achieved using diazonium salts which are covalently functionalized on the electron-rich sp^2 carbon domains of GO nanosheets [25,31,32]. Additional functional group density can be imparted to the surface (e.g., $-SH$, $-NH_2$ and $-COOH$ groups) and potentially enhance GO's performance in the adsorption of dyes and other organic compounds.

Here, we functionalize the surface of a clinoptilolite-rich natural zeolite with GO nanosheets followed by the covalent attachment of a diazonium salt, 4-carboxybenzenediazoniumtetrafluoroborate, to the GO surface. Thus producing a so-called carboxy-GO/zeolite adsorbent. The adsorption affinity, kinetics and equilibrium loading capacity of both the pristine natural zeolites and the carboxy-GO/zeolite adsorbents toward aqueous solutions of rhodamine B were investigated. We also show the impact of surface functionality, initial dye concentration, pH and dye exposure time on the adsorption of rhodamine B onto the adsorbents.

2. Experimental

2.1. Materials

Australian natural zeolite (diameter: 2 mm, chemical composition: 68.26% SiO_2 , 12.99% Al_2O_3 , 1.37% Fe_2O_3 , 0.83% MgO , and 0.23% TiO_2) was purchased from Zeolite Australia Limited (New South Wales, Australia) and ground in a mortar and pestle before use.

GO was purchased from Graphene Supermarket (BET surface area: $\sim 400\text{ m}^2\text{ g}^{-1}$), USA, and used as received. Rhodamine B (molecular weight 479.01 g mol^{-1} , CAS Number 81-88-9 and molecular structure shown in Scheme 1), 4-aminobenzoic acid, fluoroboric acid and sodium nitrite were purchased from Sigma-Aldrich (Australia). Hydrochloric acid, sodium hydroxide, acetone and ethanol were supplied from Chem Supply (Australia). All aqueous solutions were prepared using Milli-Q water ($18.2\text{ M}\Omega\text{ cm}$ at 25°C).

2.2. Acid treatment of natural zeolite powder

Zeolite powder (0.5 g) was suspended in Milli-Q water (20 cm^3). 32% (v/v) aqueous hydrochloric acid (0.1 cm^3) was added and the suspension stirred for 30 min. The resulting acid-treated zeolite powder was then separated via centrifugation at 3000 rpm for 5 min, followed by successive washings and centrifugation with Milli-Q water.

2.3. Functionalization of acid-treated zeolite powder with GO nanosheets

GO powder (5 mg) was dispersed in Milli-Q water (5 cm^3) and sonicated (Unisonics sonicator, FXP10MH) for 1 min. The GO dispersion (1 cm^3 , 40 mg dm^{-3}) was added to the acid-treated zeolite powder ($\sim 0.5\text{ g}$) in Milli-Q water (10 cm^3). The suspension was sonicated for 10 s, stirred for 30 min and then placed in an oven at 110°C for 12 h. The GO/zeolite powder was cooled to room temperature for further use.

2.4. Synthesis of 4-carboxybenzenediazoniumtetrafluoroborate (carboxy-BDTFB)

According to Blanch et al.'s procedure [33], 4-carboxybenzenediazoniumtetrafluoroborate (carboxy-BDTFB) was synthesized by dissolving 13.72 g 4-aminobenzoic acid in a mixture of 34 cm^3 48% fluoroboric acid and 40 cm^3 Milli-Q water and the solution was cooled down to 0°C . 6.8 g sodium nitrite was dissolved in 15 cm^3 Milli-Q water and was added drop-wise to the solution, stirred for 30 min. The precipitate was collected via vacuum filtration and purified by dissolving in a minimum amount

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