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Kinetics and thermodynamics of malachite green dye adsorption from aqueous solutions on graphene oxide and reduced graphene oxide

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ABSTRACT

Rapid adsorption process of hazardous malachite green (MG) dye from the liquid phase onto the developed adsorbent i.e. graphene oxide (GO) and reduced graphene oxide (rGO) surfaces was well studied and elucidated. The batch adsorption experiments were carried out in order to evaluate the optimized values of the influential parameters such as initial pH, contact time, and temperature. The obtained optimized values of pH, contact time and temperature was 3, 100 min and endothermic nature of the adsorption process. It was found that by increasing the pH value from 3 to 9, the removal of malachite green dye by the developed adsorbent i.e. GO and rGO was decreased. Additionally by increasing the temperature, the removal of noxious MG dye by GO and rGO adsorbents was increased, which directly indicates towards the endothermic nature of the adsorption process. The adsorption kinetic data of malachite green dye on GO and rGO surfaces was found to be well fitted and in good agreement with the pseudo-first-order kinetic model because of the low value of the chi-square statistic (χ^2) and high value of the correlation coefficients (R^2).

1. Introduction

Wastewater treatment nowadays weighed as a large area of research because this is an important universal concern due to the sudden decrement in the reservoirs of fresh drinking water. The obviation of contaminants from the aqueous phase is a principal environmental subject matter because of their broad applications in several industrial activities many industrial effluents including textile companies, plants, food producers, dye factory and electroplating factories, release wastewater containing dyes and thereby contaminate water resources [1]. Textile dyeing effluents are composed of complex mixtures of dye bases, acids, salts, auxiliary chemicals, compounds, organ chlorinated and occasionally heavy metals [2]. These noxious dyes lead to several severe and detrimental health problems such as dermatitis, allergy, and skin irritation and also provoke mutation and cancer in humans [3]. Therefore a keen attention and serious effort of researchers are required to eradicate this problem or to find the natural convenient way for the pre-treatment of the noxious dye effluents [4–5].

Malachite green (MG) dye is one of the organic compounds that has emerged as a controversial agent in the aquaculture and is used as a dyestuff. Malachite green dye is traditionally used as a dye for materials such as leather, silk and paper [6,7]. For the removal of noxious dyes various treatment methods and materials were applied such as membrane filtration, photocatalyzed degradation, microbiological, oxidation, ozonation, adsorption, coagulation/flocculation, and degradation by biological processes [8–39]. Adsorption at the liquid phase has a major advantage over other methods due to its high efficiency in the removal of toxic pollutants, easy operation and low cost [40].

In the present work, we investigated the adsorption capacity of malachite green dye on graphene oxide and reduced graphene oxide. Kinetics study showed that adsorption of malachite green dye on GO and rGO surfaces was well interpreted by the pseudo-first-order kinetic model. For all adsorption experiments optimum time was determined at 100 min at 298 K and pH 3. Result of the effects of temperature showed that the adsorption processes of malachite green dye onto the developed adsorbents i.e. GO and rGO was endothermic in nature.

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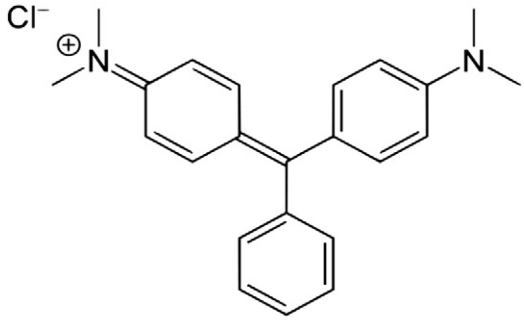

Fig. 1. Chemical structure of malachite green dye molecule.

2. Materials and methods

2.1. Materials

To investigate the adsorption capacity of malachite green dye on graphene oxide and reduced graphene oxide, we used single layer graphene oxide with specifications: aqueous dispersion: 175 mL, concentration: 500 mg/L, composition: carbon (79%), oxygen (20%), flake size: 0.3–0.7 μm, thickness: 1 atomic layer — at least 80% and color: brown and reduced graphene oxide with pacifications: specific surface area—833 m^2/g, solid content: 98%, carbon/oxygen ratio 10.5, average flake thickness: 1 monolayer and average particle (lateral) size: ~3–5 μm were used at all adsorption experiments as adsorbents that were prepared from a graphene supermarket, USA.

Malachite green dye (Fig. 1) (MG: $[C_6H_5C(C_6H_4N(CH_3)_2)_2]Cl$) molecular weight: 364.911 g/mol was prepared from the commercial manufacturing company Dy Star Co. (Germany) of 90% purity. During all the adsorption experiments de-ionized water was used as solvent for preparation dye solution.

2.2. Preparation of GO and rGO surfaces

The adsorbent i.e. graphene oxide and reduced graphene oxide surface used to carry out the adsorption experiments were prepared from the graphene that was obtained from a supermarket, USA.

2.3. Batch adsorption study

20 mg of graphene oxide and reduced graphene oxide as adsorbents into 20 mL dye solutions with known concentration of 25 mg L^{-1} was added during all the adsorption experiments. After a certain period of time at 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110 and 120 min the samples were collected and the concentration of dye in the aqueous solutions was determined by using the UV–Vis spectrophotometer furnished by Varian (Cary 100 Bio) (London, England). Then for kinetic study dye adsorption capacity at time t (qt), in mg/g, was calculated using Eq. (1) [41].

$$q_t = \left(\frac{C_0 - C_t}{W}\right) \times V \qquad (1)$$

where q_t (mg/g) was malachite green adsorption capacity at time t, C_0 (mg L^{-1}) was the initial malachite green concentration and C_t (mg L^{-1}) was the malachite green concentration at time t, V was the volume (L) of dye solution and W was adsorbent mass (g). Adsorption time curve for malachite green adsorption on GO and rGO as adsorbents shown in Fig. 3 was calculated using

$$q_t = \left(\frac{C_0 - C_e}{W}\right) \times V \qquad (2)$$

where C_0 and C_e are the initial and equilibrium dye concentrations (mg/L) [42] (Fig. 1).

3. Result and discussion

3.1. Characterizations of GO and rGO

The morphological and anatomical facade of the developed adsorbent i.e. graphene oxide (GO) and reduced graphene oxide (rGO) study was carried out using the surface electron microscopy, and the morphological and anatomical features of the surface were well investigated and elucidated. The textural properties obtained during the study were shown in Fig. 2. The obtained results revealed the formation of the microstructures on the textural surface of the developed adsorbent.

3.2. Effect of contact time

Equilibrium studies were investigated at pre-fixed time intervals, ranging from 10 to 120 min, in order to determine the optimal time for the adsorption. Fig. 3 shows that the equilibrium state was established within 100 min. At this point, the amount of dye desorbing from the adsorbent is in a state of dynamic equilibrium with the amount of dye being adsorbed onto the adsorbents. Consequently, 100 min will be the contact time used in our adsorption experiments.

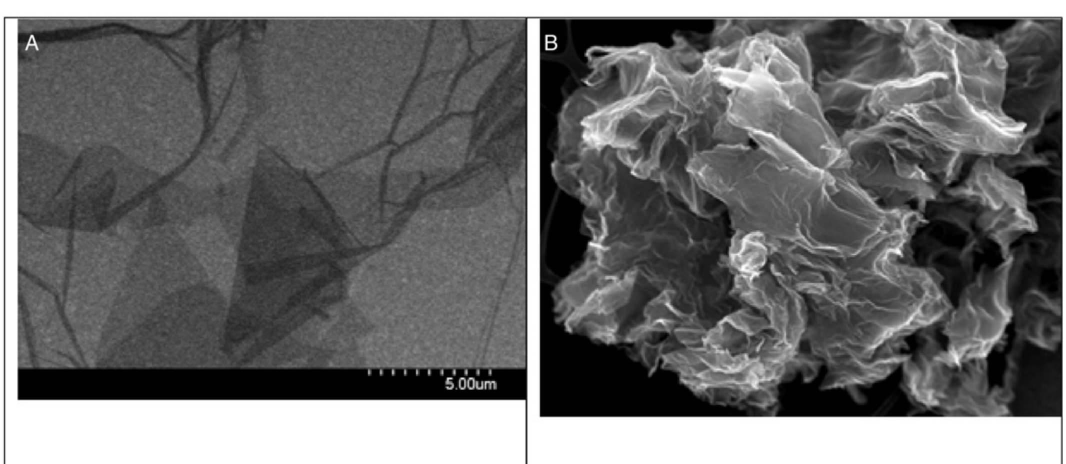

Fig. 2. SEM images of adsorbents. (A) Single layer graphene oxide surface, (B) reduced graphene oxide surface.