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# Highly efficient removal of Malachite green from water by a magnetic reduced graphene oxide/zeolitic imidazolate framework self-assembled nanocomposite

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ABSTRACT

Compared to the relatively low adsorption capacities of conventional adsorbents for Malachite Green (MG) (*i.e.*, ~500 mg $g^{-1}$), zeolitic imidazolate framework (ZIF) appears to be a promising adsorbent considering its significantly high adsorption capacity (*i.e.*, >2000 mg $g^{-1}$). Nevertheless, using such a nano-scale ZIF material for adsorption may lead to secondary contamination from the release of nanomaterials to the environment. Thus, ZIF has to be recovered conveniently to prevent the secondary contamination and facilitate the separation of adsorbent from water after adsorption. To this end, in this study ZIF nanocrystals were loaded on the sheet-like magnetic reduced graphene oxide (MRGO) to form a self-assembled MRGO/ZIF. The self-assembly of MRGO/ZIF was achieved possibly *via* the electrostatic attraction and the π–π stacking interaction between MRGO and ZIF. The resultant MRGO/ZIF exhibited an ultra-high adsorption capacity for MG (~3000 mg $g^{-1}$). The adsorption kinetics, isotherm, activation and thermodynamics were also determined. Other factors affecting the adsorption were examined including temperature, pH and co-existing ions/compound. To demonstrate that MRGO/ZIF can be recovered and reused, a multiple-cycle of MG adsorption using the regenerated MRGO/ZIF was revealed and the recyclability remained highly efficient and stable. The highly-effective, recoverable and re-usable features enable MRGO/ZIF a promising adsorbent to remove MG from water.



## 1. Introduction

Malachite green (MG) is a common dye in textile industry [1]. MG can be also used as a disinfectant and an antifungal agent, particularly, for aquaculture [2,3]. The exposure to MG, however, is considered to cause carcinogenesis, mutagenesis, teratogenesis and respiratory diseases [3]; thus it is essential to remove MG from water in order to avoid the exposure to MG.

Up to date, MG can be removed from water *via* several methods including coagulation/flocculation [4], biological decolorization [5,6] and adsorption [7–11]. Coagulation/flocculation, nevertheless, is ineffective to treat MG-containing wastewater because of high solubility of MG in water [7]. On the other hand, the biological decolorization typically requires long operation time [12] and dyes can be resistant to biodegradation [13]. Considering these issues, adsorption appears to be a more feasible method to remove MG because adsorption process is easy to implement and scale up with low initial cost [14,15]. Therefore, many adsorbents have been reported to remove MG from water and most of them are waste-derived activated carbon [7–11], chemically modified biomass [16], ordered mesoporous carbon [17] and graphene oxide [18]. These conventional materials generally exhibited quite limited adsorption capacities (*i.e.*, ~500 mg $g^{-1}$).

Recently, a novel inorganic-organic hybrid material, zeolitic imidazolate framework (ZIF)-67, has been proposed as an adsorbent to remove MG from water and ZIF showed significantly high adsorption capacity for MG (*i.e.*, >2000 mg $g^{-1}$) [19]. Although ZIF seems to be a promising adsorbent to remove MG, such a nano-scale material has to be recovered after the adsorption process to avoid its release to the environment. However, to our best knowledge, almost no ZIF with recoverability has been developed for the MG adsorption. Thus, this present study proposes to prepare a highly efficient and recoverable adsorbent incorporating with ZIF. To load ZIF on a controllable substrate, we particularly adopted a magnetic reduced graphene oxide (MRGO) as a support. MRGO was selected because it can be prepared from a one-pot synthesis

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hydrothermally [20] and its sheet-like structure can provide large planar surfaces to load ZIF. *Via* a simple mixing of MRGO and ZIF, a self-assembled MRGO/ZIF nanocomposite can be obtained, which can be magnetically controllable, allowing MRGO/ZIF to be recovered conveniently.

Characteristics of the as-prepared MRGO/ZIF were determined, including morphology, surface charge, crystalline structure, surface chemistry and conjugated carbon bonding. To examine the magnetic property of MRGO/ZIF, a magnetometer was also used, while thermogravimetric analyzer (TGA) was adopted to reveal its thermal decomposition behaviors. The MG adsorption kinetics and isotherm using MRGO/ZIF were measured and analyzed by theoretical models. Adsorption activation energy and thermodynamics were also determined to probe in the adsorption mechanism. Factors affecting the MG adsorption were also investigated, such as temperature, pH and co-existing ions/compounds. Recyclability of MRGO/ZIF for the MG adsorption was examined and a multiple-cycle of MG adsorption using the regenerated MRGO/ZIF was demonstrated.

## 2. Experimental

### 2.1. Materials

All chemicals used in this study were purchased from commercial chemical suppliers.

Graphite was from Showa Chemicals (Japan). 2-methylimidazole (2-MIM) and cetyltrimethylammonium bromide (CTAB) were from Acros Organics (USA). Malachite green dye and cobalt nitrate were obtained from Choneye Pure Chemicals (Taiwan). Iron sulfate ($Fe(SO_4)$) and glucose were from Sigma-Aldrich (USA). Deionized (DI) water was prepared to exhibit less than 18 MOhm-cm.

### 2.2. Synthesis and characterization of MRGO/ZIF

Preparation of MRGO/ZIF can be illustrated as Fig. 1a. First, MRGO was synthesized based on the reported protocol [20]. In brief, GO (100 mg), prepared according to Hummers' method [21], was added to 50 mL of DI water and sonicated for 1 h, followed by addition of 100 mg of glucose and 1 mL of $NH_4OH$ solution. On the other hand, 100 mg of $Fe(SO_4)$ was added in 5 mL of DI water, to which 20 mg of NaOH in 5 mL of ethanol was subsequently added. The resultant GO suspension was mixed with the ferrous solution for 30 min and then the mixture was transferred to a Teflon-lined autoclave and heated at 180 °C for 12 h. The precipitate was collected, washed with DI water and dried at 65 °C for 12 h to obtain MRGO. To prepare MRGO/ZIF, 0.36 g of $Co(NO_3)_2$ and 1.32 g of 2-MIM were added to 150 mL of DI water and stirred at ambient temperature for 2 h to obtain a ZIF (*i.e.*, ZIF-67) suspension. Next, 1.6 g of MRGO was sonicated in 200 mL of DI water for 30 min and the resultant MRGO suspension was added to the ZIF suspension and the resultant mixture was stirred for 12 h at ambient temperature. The self-assembled nanocomposite was collected using a permanent magnet, and then washed and dried to yield the final product, MRGO/ZIF.

MRGO/ZIF was first characterized using a TEM (JEOL JEM-2010, Japan) to reveal its morphology. Surface charges of MRGO/ZIF and precursors were measured in water by a zetasizer (Nano-ZS, Malvern Instruments Ltd, Malvern, UK). Crystalline structures of MRGO/ZIF and precursors were determined using an X-ray diffractometer (BRUKER D8 DISCOVER). IR spectra were obtained by an infrared spectrometer (Jasco 4100, Japan). Conjugated

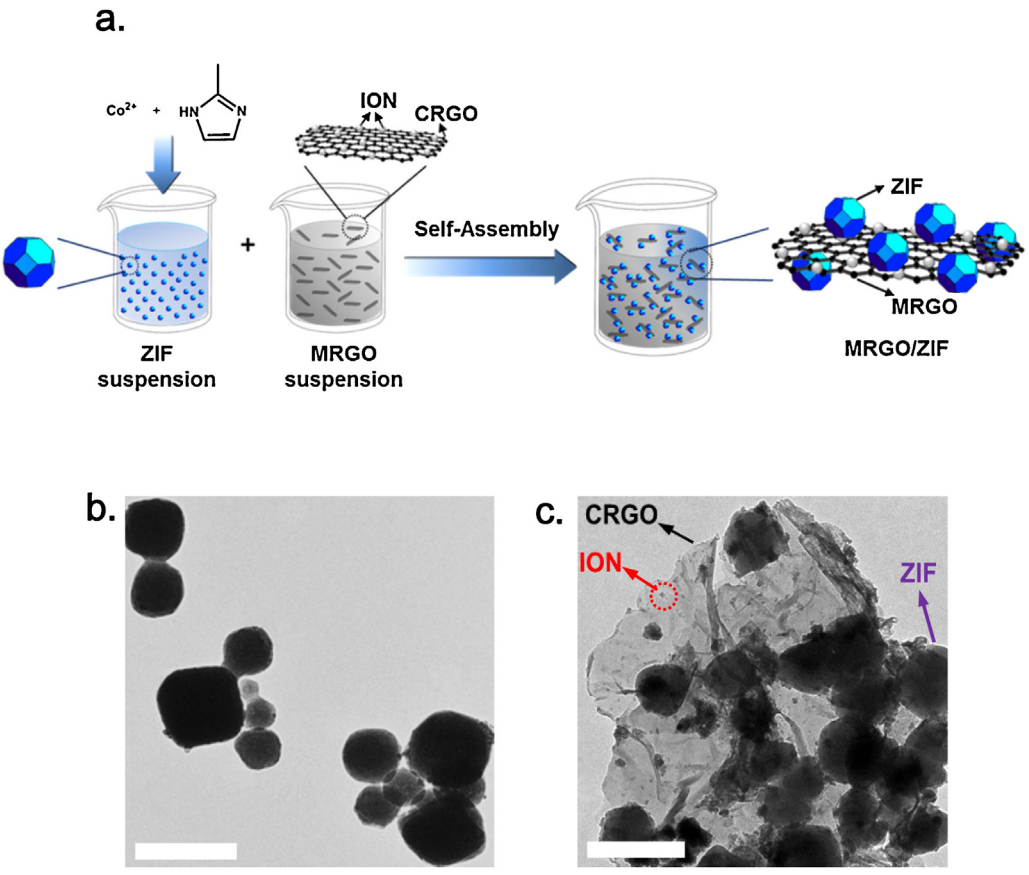


**Fig. 1.** MRGO/ZIF: (a) synthesis scheme, (b) a TEM image of the precursor, ZIF-67 and (c) a TEM image of MRGO/ZIF (scale bar = 500 nm).