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# Kinetic, isotherm and thermodynamic studies for removal of methyl orange using a novel β-cyclodextrin functionalized graphene oxide-isophorone diisocyanate composites

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ABSTRACT

A novel β-cyclodextrin functionalized graphene oxide-isophorone diisocyanate composite (GO-IPDI-CDs) was prepared with graphene oxide (GO), isophorone diisocyanate (IPDI) and β-cyclodextrin (β-CD) as raw materials. The structure and morphology of GO-IPDI-CDs were characterized by Fourier transform infrared spectroscopy (FT-IR), Brunauer–Emmett–Teller (BET), Raman, scanning electron microscopy (SEM), X-ray diffractometer (XRD) and thermogravimetric analysis (TG). The GO-IPDI-CDs was applied to deal with wastewater solution containing dye of methyl orange. The effects of environment factors (such as temperature, pH and so on) to methyl orange adsorption were investigated in details. The results showed that GO-IPDI-CDs has a highest adsorption efficiency of 92.88% and adsorption capacity of 83.40 mg/g at the optimum conditions (0.020 g/mL of dosage of GO-IPDI-CDs, temperature of 45 °C, a time of 2.5 h and pH = 6.0). Adsorption kinetics, adsorption isotherm and adsorption thermodynamic were investigated. Pseudo second-order kinetics equation can describe the adsorption process appropriately. Langmuir and Freundlich isotherm models were used to simulate the equilibrium data and the results showed that the equilibrium data were close to Langmuir model. The thermodynamic parameters indicated that the adsorption process was endothermic. The proposed method has been successfully applied to adsorb methyl orange in water samples with satisfactory result.


## 1. Introduction

All kinds of synthetic dyes are commonly used in textile, cosmetics and other industries. Recently, loading of wastewater treatment systems with dye chemical runoff from urban areas has become a serious problem. Dye chemicals can absorb light, which will reduce the water transparency, affect aquatic organisms and microbes and go against water self-purification. A large amount of wastewater containing dyes is discharged without effective treatment in the process of production and use of dyes, which brings about a serious pollution to the environment and harms human health. Most of those dyes cannot be treated effectively by traditional biodegradation and conventional chemical oxidation because of stable complex aromatic molecules. Therefore, the treatment of dye wastewater effectively is very important to reduce dye wastewater emissions and protect the aquatic environment.

Current approaches of dye removal, such as traditionally biological, physical and chemical techniques, in depth degradation, cost control and harmless processing, are still

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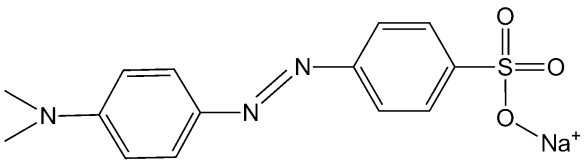


**Fig. 1 – The structure of methyl orange (MO).**

far from satisfactory. Thus, the satisfied treatment of dye wastewater has been a hot topic of environment field. As a low-cost and convenient method, adsorption is very promising for the removal of azo-dyes from wastewater, and it is widely used in water treatment (Chen et al., 2015). Methyl orange (MO) solution, as the main representative of dye compounds, is main structure of dye compounds (Fig. 1). Deligeer et al. (2011) prepared mesoporous γ-$Fe_2O_3$/$SiO_2$ nanocomposite for removal MO and the adsorbed percentage was 83%. Tanhaei et al. (2015) reported that the prepared chitosan/$Al_2O_3$/magnetite nanoparticles composite for removal MO had the adsorption rate of 93%. Obeid et al. (2013) synthesized chitosan/maghemite composite for the adsorption of MO and the adsorption rate reached 90%. Asuha et al. (2010) reported that mesoporous $TiO_2$ for the adsorption of MO had the adsorbed percentage of 87%.

An excellent adsorbent should readily available and rarely have toxic. Moreover, it is stable under various conditions and should have high adsorption ability. In general, the adsorption capacity of an adsorbent mainly depends on its surface properties including surface area and surface ion exchange sites (Deligeer et al., 2011). Cyclodextrins (CDs) are cyclic oligosaccharides including glucose units linked by α-1,4-glucosidic bonds (Zhang et al., 2013), which has a hydrophobic inner cavity and a hydrophilic exterior (Fan et al., 2013). α, β and γ-CDs are the most commonly used, which contain six, seven, eight pyran-glucose units and have cavity structure (Jiang et al., 2010). It shows the features of Lewis base, as the unpaired electron of oxygen which is pointing to the inside of the cavity makes the electron cloud density of the cyclodextrin higher. Each glucose unit of CD has five chiral carbon atoms. Due to special cavity structure of CD, which constituted a kind of non-polar micro-environment to allow a number of small object organic molecules and inorganic ions to enter, so it can package multiple object molecules to form a supramolecular complexes. CD has certain rigidity because of the edge of the hydroxyl formed hydrogen bond network; object molecules match with cavity size can play an extremely important role in the stability of the main-the object complexes. Furthermore, CDs are environmentally friendly, water-soluble, and can improve the solubility and stability of functional materials. CDs can be attached on the surface of reduced graphene oxide (RGO) sheets by the strong hydrogen bonding to make graphene more hydrophilic (Guo et al., 2010).

β-Cyclodextrin (β-CD) has been widely used as a dispersing reagent for insoluble chemicals and nanomaterials, including carbon nanotubes (Alarcón-Angeles et al., 2008; Liu et al., 2008). β-CD polymer (CDP) has been obtained by the reaction of β-CD with a cross linking agent, epichlorohydrin (Zhang et al., 2013). β-CD has moderate 0.6 nm cavity diameter and low production cost and is currently the only mass production on industrial and application widely. In addition, β-CD can show high molecular selectivity and enantioselectivity (Freeman et al., 2009) and improve the solubility and stability of functional materials (Wei et al., 2014).

Graphite is a kind of laminated material, which is formed by the layered network of two-dimensional carbon plane. The force between carbon layers is weak, so it's easy to separate from each other between graphite layers to form a very thin layer of graphite structure. It will be the graphene when graphite is separate layer by layer to only one carbon atom formation thickness of single layer of graphite (Novoselov et al., 2004). The special nanostructures of graphene show that it has special excellent mechanical, electrical and optical properties. The way of carbon atoms in graphene bonding is $sp^2$ hybridization. Graphene has strong plane carbon–carbon bond, and the out-of-plane each $\pi$ bond together to form the domain of "π", it makes π electrons to move freely in its surface to form of delocalized electrons (Kuila et al., 2010; Li et al., 2013); and it is expected to play an extremely important role in the manufacture of bio-electronic and nano-electronic devices in near future (Geim and Novoselov, 2007). Although graphene has a unique structure, using chemical method make graphite oxidation to graphene oxide (GO) is more popular. GO is a kind of important derivatives of graphene, it is also named functionalized graphene and has same structure as graphene. It has been reported that GO is an excellent adsorbent in removing dye in aqueous solutions; and includes many oxygen-containing functional groups on the surfaces, such as —OH, —COOH (Zhao et al., 2012). These functional groups make GO to be chemical modification easily, but it's difficult to be separated from water solution.

In this work, a novel composite material (GO-IPDI-CDs) was prepared. The structure and morphology of GO-IPDI-CDs were investigated by FT-IR, BET, Raman, SEM, TG and XRD. The adsorption properties of GO-IPDI-CDs toward methyl orange (MO) adsorption were studied using equilibrium, kinetic and thermodynamics. Best of our knowledge, this is the first time that the obtained GO-IPDI-CDs is reported.

## 2. Experimental details

### 2.1. *Materials*

Graphite powder, concentrated sulfuric acid ($H_2SO_4$), sodium nitrate ($NaNO_3$), potassium permanganate ($KMnO_4$), concentration of 30% hydrogen peroxide ($H_2O_2$), hydrogen chloride (HCl), sodium hydroxide (NaOH), dibutyl tin laurate (T-12), isophorone diisocyanate (IPDI, purity ≥ 99.5% and —NCO content ≥ 37.5%), *N*,*N*-dimethyl formamide (DMF)and β-Cyclodextrin (β-CD) was purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Methyl orange (MO) was obtained from three reagent factory in Shanghai.

### 2.2. *Preparation of graphene oxide (GO)*

GO was prepared by Hummers method (Hummers and Offeman, 1958), and its preparation process as follows: 230 mL, the concentration of 98% $H_2SO_4$ was added in beaker with ice water to 4 °C or so, 10 g graphite powder and 5 g $NaNO_3$ were add in constantly stirring. Vigorous stirring, and then 30 g $KMnO_4$ powder was added slowly, at the same time, control temperature below 20 °C, when all $KMnO_4$ powder was added, feedback to the ice water bath and raise the temperature to 35 °C with constantly stirring for 30 min, then added 460 mL water gradually and made the temperature rise to 98 °C. Maintain for 15 min at this temperature, and then diluted with warm water to 1400 mL. Strike filter after adding 100 mL $H_2O_2$