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Microwave-assisted removal of malachite green by carboxylate functionalized multi-walled carbon nanotubes: Kinetics and equilibrium study

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ABSTRACT

Carboxylate group functionalized multi-walled carbon nanotubes (MWCNT–COOH) were synthesized by microwave-assisted method and characterized by Infrared spectroscopy; XRD methods and scanning electron microscope (SEM). These were used as adsorbent for the rapid removal of hazardous toxic dye Malachite green (MG) from aqueous phase. The impact of several effective parameters such as contact time, temperature, initial concentration, and agitation speed was investigated and the optimized values of influential parameters like pH, contact time, temperature, initial concentration, and agitation speed on experimentation were found to be 6, 50 min, 298 K, 15 mg/L and 150 rpm respectively. The experimental kinetic data were well fitted to the pseudo-first order reaction kinetics and results. Different adsorption isotherm models like Freundlich, Langmuir and Temkin are used to describe equilibrium adsorption in the adsorbent system and on experimentation the best agreement was achieved with the Langmuir model, for MG, the adsorption capacity of MWCNT–COOH surface was 49.45 mg/g at 298 K.

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1. Introduction

Several hazardous and toxic dyes are extensively used in the synthesis, printing, textile, pulp mill, food and cosmetic industries. Synthetic dyes are toxic as well as noxious, hence they must be removed immediately from aquatic sources, and otherwise they will lead to severe detrimental effect on the individual health and on the sustaining diversified flora as well as aquatic fauna. The estimated twelve-monthly production of commercially available dyes is approximately 7×10^5 t, which includes more than 100,000 kinds of toxic and hazardous dyes [1]. It has been reported that about 10–15% of the dye concentration is released to the ecosystem and biome after the dyeing process [2,3]. As a result a keen attention and successful remediation plan is required to control the toxic dyes effluent discharge and especially more concerned is needed for designing the technical treatment scheme of this hazardous discharge [4,5]. Malachite green belongs to the same group of triphenylmethane dyes as crystal violet, in which carcinogenic effects have been demonstrated. Based on the same group classification, a carcinogenic effect can be assumed, it was demonstrated that the tested substances showed affinity to the liver, thyroid gland and bladder, where morphological changes were observed. Laboratory tests also demonstrated that malachite green may damage DNA after in vitro metabolic activation, although no genotoxicity was demonstrated in in vivo tests [6]. In recent years, many methods were proposed and implemented to remove the noxious dyes from wastewater, such as physical separation, chemical oxidation and biological degradation [7–9]. In addition to previously mentioned methods, the adsorption process possess a significant role and have been widely used for rapid removal of toxic, noxious dyes and other hazardous impurities [10]. Adsorption is considered as a most efficient technique for the quick removal of dyes from polluted aquatic sources, since it is a simple, non-destructive and easy to apply technique [10]. Several previously developed adsorbents such as activated carbon [11,12], zeolites [13], carbon nanotubes [14–33], MWCNTs [34,35], nanoparticles and nanocomposites [36–39], lignin [40,41], rubber tire [42,43], polymers [44] and other lost adsorbents [45–50], have been extensively used for instantaneous removal, maximum adsorption of dyes and other noxious impurities [51–55]. Therefore, developing an effective adsorbent now a day is of great concern and the center of attention for the different

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research groups, so that the developed adsorbent may lead to rapid removal of toxic impurities within few minutes of application.

Recently, the application of carbon nanomaterials in wastewater treatment plants has gained a significant attention for their specific advantages like large surface areas and more activated functionalized sites [56]. Among them, CNTs can be visualized as graphitic carbon sheets rolled into hollow cylinders with nanometer scale diameters and micrometer scale lengths [57–59]. Owing to their unique properties, the production and chemical variations of CNTs has been growing exponentially [60], these chemical variations are created by the unique bonding configurations of carbon that make it a ubiquitous part of our environment. The one dimensional structure of the CNT was responsible for the high surface area, the ability to act as a semiconductor or a metal, the existence of multiple direct band gaps, the relative ease of attachment for numerous chemical functional groups, and the ability to decorate CNTs with nanoparticles [61,62]. The modified CNTs can be categorized into two groups according to the mechanism of functionalization and way of modification of CNTs. In the first, some C═C bonds are fully opened, forming defects within the CNT wall; on the other hand in the second, some C═C bonds are broken and formed single bonds are used for functionalization, resulting in yielding some sp^3 character of particular C atoms. The oxidation of carbon surfaces is known to generate not only more hydrophilic surface, but also more oxygen containing functional groups to increase the ion-exchange capacity [63]. The first type of functionalization typically involves oxidation using acids or oxidants, causing carboxyl groups to functionalize the defects of the CNTs [64], and in the second type of CNT functionalization, generally there is an addition of a C═C double bond by alkylation, arylation, oxycarbonyl nitrene, and 1, 3 dipolar cyclo-addition [65], such reactions are in general time consuming, and will complete in 15–16 h or even days.

In the present work, functionalized MWCNT–COOH was synthesized in the assistance of microwave and characterized by using scanning electron microscopy (SEM) and X-ray diffraction (XRD). The impact of influential parameters i.e. contact time, temperature, initial concentration, and agitation speed was studied.

2. Experimental

2.1. Chemicals and reagents

MWCNTs were purchased from NanoAmor Nanostructured & Amorphous Materials, Inc., USA (Purity, >95%; outer >50 nm; length, 500–2000 nm; surface area, ~40 m^2/g; and the manufacturing method, catalytic chemical vapor deposition (CVD)). All supplementary chemicals were of analytical grades and were purchased from Merck Inc., USA. Malachite green, $C_{23}H_{25}ClN_2$ (MG), a green crystalline powder with a molecular weight of 364.911 and $\lambda_{max} = 618$ (nm) (Fig. 1) was purchased from LABCHEM and was used without any further purification. All solutions were prepared with deviations of less than $\pm 0.1\%$ from the desired concentrations; their concentrations were measured by using UV–vis spectroscopy (UV-2550 SHIMADZU, Japan).

2.2. Microwave-assisted synthesis of MWCNT–COOH

Synthesis of MWCNT–COOH is very well defined and can be illustrated from Fig. 2. Microwave-assisted technique plays a crucial role in the adsorption process, it is regarded as greening pretreatment, [66,67] which was extensively used to activate or accelerate the process of chemical reaction like functionalization [68,69]. In brief, an aliquot of 100 mg pristine MWCNTs was acidified using 5-mL HNO_3 as oxidant and then treated with microwave radiation, all reagents are irradiated by placing in closed-Teflon bottles inside a microwave apparatus (MARS-Xpress, CEM, USA) operated at 600 W power and 160 °C operating temperature for 30 min. Oxidation of MWCNTs took place, resulting in MWCNTs functionalized with carboxylic groups (namely MWCNTs–COOH).

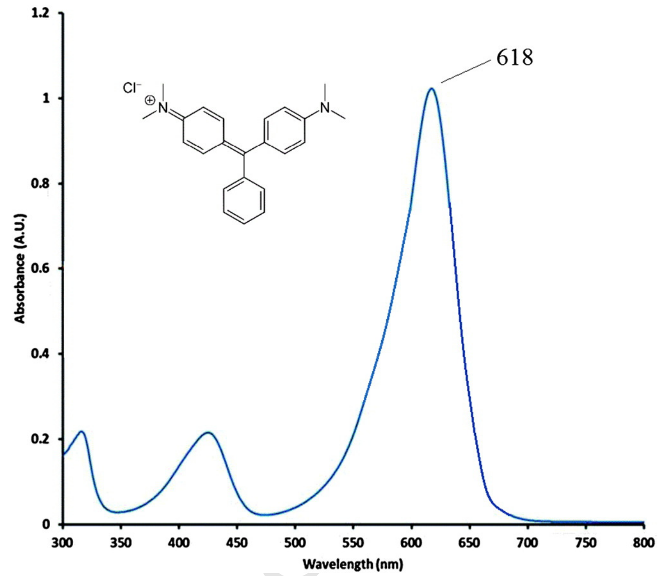

Fig. 1. Chemical structure and UV–vis spectra of Malachite green (MG).

2.3. Characterization methods

The characteristic functional groups of the MWCNT–COOH were analyzed by the attenuated total reflection–Fourier transform infrared spectrometer (100 spectra accumulation, 2 cm^{-1} resolution, BOMEM, Canada). A FT-IR sample was prepared by grinding dried MWCNT–COOH together with potassium bromide to make a pellet, which was dried in an oven for 8 h before the test. A surface textural and morphological analysis was carried out using a scanning electron microscope (SEM), (TESCAN, VEGA 3, USA(. Transmission electron microscopy (TEM) analysis was performed using a JEOL JEM microscope (TEM, JEOL 2010, Japan) operating at 200 kV by depositing sample onto the lacey carbon-coated copper grids.

2.4. Adsorption experiments

Tests was carried out within the 100 mL conical flasks containing 50 mL MG solution in a distilled water, to elucidate the values of the test parameters including solution pH (1–11), dye concentration (50–200 ppm), temperature (298 K), contact time (0–180 min), agitation speed (0–150 rpm) and 0.05 g of adsorbent. After each removal of condition experiments, the sample was centrifuged (2000 rpm, 20 min) using a centrifuge (Hettich, EBA 21, Germany) for separation of

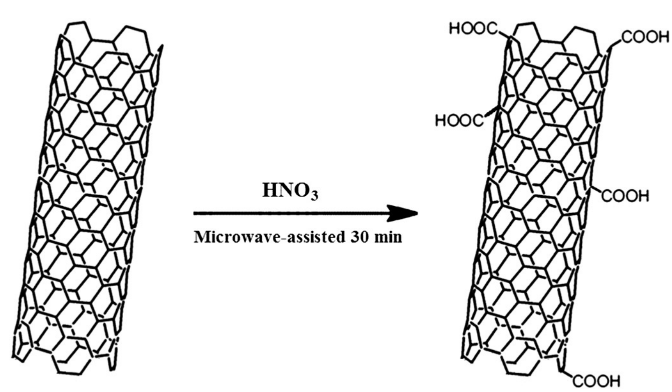

Fig. 2. A diagram for synthesis of MWCNT–COOH.

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