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RESEARCH ARTICLE

Enhance Photo Degradation of Methylene Blue Dye in The Presence of MOF Of Indium Doping with Graphene Oxide

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Abstract

The environment and human health are seriously threatened by water contamination, especially that caused by industrial dye effluents. Methylene Blue (MB), one of the many dyes, is used extensively in the chemical and textile industries and is well-known for being poisonous and persistent. In order to tackle this problem, adsorbents based on porous catalysts have been investigated more for efficient dye removal. Here, we report the effective solvothermal synthesis of a porous indium-based metal- organic framework (MOF), called AUBM-1, utilizing indium nitrate as the metal precursor. When compared to standard commercial adsorbents, the activated AUBM-1 demonstrated improved methylene blue dye adsorption ability. Graphene is used as a dopant so its dye degradation properties can be increased. XRD confirms its crystalline structure and presence of indium and graphene. The morphology structure of the composite is observed under field-emission scanning electron microscopy (FESEM) which proves successful incorporation of such a MOF with graphene. The composite, i.e., indium-based MOF and graphene oxide (GO), showed outstanding removal of dye, with a value of

close to around 99%. GO alone showed high adsorption capacity and had adsorbed 85.78 percent of the dye in 40 minutes which is suitable for waste water treatment.

Keywords: Metal-Organic framework (MOF), Graphene Oxide (GO), Methylene Blue (MB), Indium nitrate Metal-Organic framework (AUBM-1), Photo-catalyst.

Introduction

Rapid population growth and industrialization contribute to the water pollution that is one of the significant environmental threats. Issue of releasing organic dyes like methylene blue (MB) is a key issue of concern since they are mainly utilized by both textile, leather and dye making industries. These contaminants play a key role in water pollution and hence there is a need to have efficient removal technologies [1]. Photocatalysis is a method that is used for water splitting, dye removal, hydrogen production, CO_2 conversion, and solar energy conversion. Over the last year researchers have worked on many photocatalysts like TiO_2, CdS, and ZnO, but unstable, poor recyclability is a problem with these materials [2]. The potential alternative provides a carbon-based material such as graphene that is cost effective and demonstrates excellent cycling capabilities. However, graphene on its own has a low photocatalytic activity under visible light which limits its application.MOF-based materials are gaining interest for the dye degradation process due to their high surface area and tunable structure. They show a significant effect on Congo red and methylene blue dye; however, their weak binding forces limit performance. A GO in MOF hybrid composite was made to improve the functionality of the MOF. This resulting composite has a better stability and has a high adsorption capacity of removing dye molecules in aqueous solutions [3]. Silvia Dimova et al. observed that a photocatalyst system comprising a poly(diphenylacetylene)-zinc oxide (PDPA-ZnO) embedded in a polystyrene (psEY) matrix obtained a degradation efficiency of 88% under visible light, which was much higher compared to undoped converter PDPA-ZnO. This improvement was explained by the existence of synergistic effects and π- π interactions [4]. Moreover, the utilization of NNU-36 as a highly successful heterogeneous photocatalyst in the reduction of aqueous Cr(VI) and the deterioration of organic dyes, such as rhodamine B (RhB), rhodamine 6G (R6G), and methylene blue (MLB) has recently been proved by Xing et al [5]. The analysis of AgTz-1 MOF in the adsorption of dye molecules in aqueous solution were carried out. Initial experiments showed that AgTz-1 could successfully absorb a small anionic dye methyl orange (MO). But, its adsorption capacity decreased greatly against bigger or cationic dyes, e.g., methyl blue (MB), MLB and RhB. This preference highlights the playing role of molecular size and charge in MOF-based and adsorption processes.

This research focuses upon a heterogeneous MOF@graphene oxide (GO) composite capable of the degradation of methylene blue (MB) under visible light activation conditions resulting in complete degradation achieved in 80 minutes. The composite is cost effective and environmentally compatible and hence a potential candidate to be used in the purification of water. Its effective performance indicates that it can be applied at an industrial scale in industrial wastewater treatment processes that aim at removing dyes.

Results and Discussion

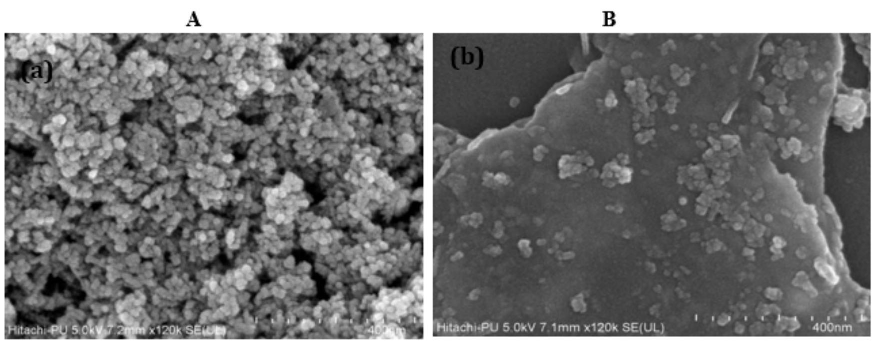

Figure 1: a) FESEM Image of (a) MOF b) InMOF/GO Composite.

Porous indium-based metal-organic framework (MOF) and GO+MOF hybrid structure synthesized via solvothermal method, utilizing indium nitrate as the metal precursor (Supplementary data). Field Emission Scanning Electron Microscope (FESEM) is utilized to study morphology of MOF and MOF/GO hybrid structure as shown in Fig 1. MOF and MOF/GO was visible at magnification of 25000x at 5kV of accelerating voltage. The pure MOF is in a form of spheres whereas MOF/GO is characterized by MOF having dispersed particles on graphene oxide sheets. Although, GO generally shows a layered structure, the combination process and subsequent heating process causes partial reduction of GO achieving the shorter interlayer spacing and loss of the distinctive layered structure [6]. FTIR study was performed in range from 400 cm^{-1}- 4000cm^{-1}. The spectrum is displayed in Fig. 2

(a). In case of MOF, the absorption peaks were observed at 778cm^{-1}, 1027 cm^{-1}, 1252 cm^{-1}, 1394 cm^{-1}, 1560 cm^{-1}, 1655 cm^{-1} and 3332 cm^{-1} attributing to In-O, C-O-C, C-OH, O-H, bond stretching vibrations of –COOH functional group. In MOF/GO peaks were observed at 769 cm^{-1}, 1059 cm^{-1}, 1362 cm^{-1}, 1562 cm^{-1}, 3320 cm^{-1}can be ascribed with doping of GO in MOF peaks slightly shift due to change its morphology (shown in fig 2.). Fig.2 (b) displays the XRD pattern of the pristine metal- organic framework (MOF), showing prominent diffraction peaks at 10.4°, 18.3°, and 28.2°, which correspond well with the standard pattern for MIL-68(In), as confirmed by the JCPDS card No. 00- 064-0994. Fig.2(b) represents the XRD pattern of the graphene oxide (GO)-doped MOF composite (MOF@GO).

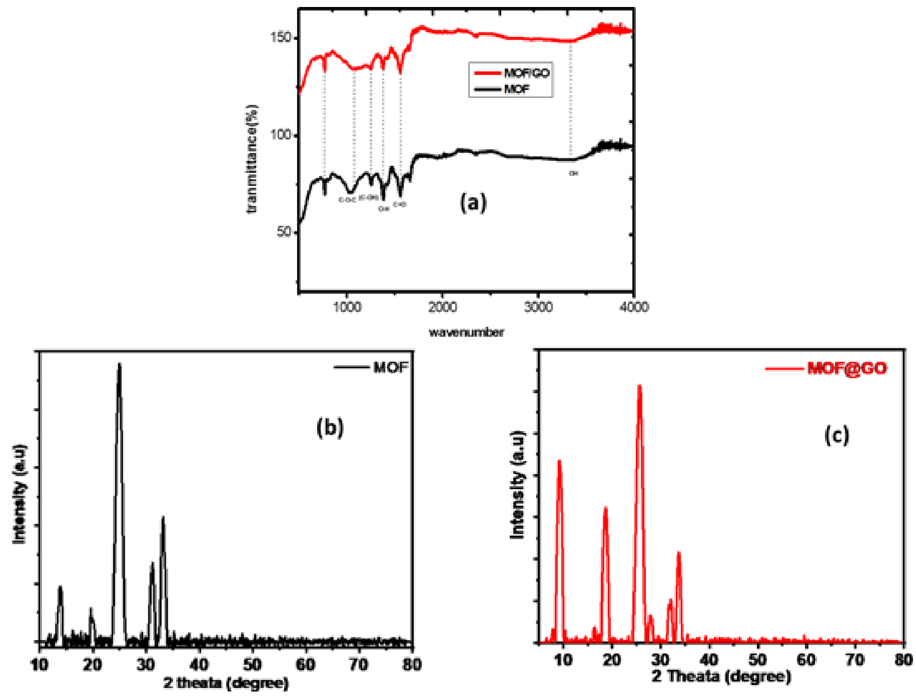

Figure 2: (a) FTIR spectra of MOFs and MOF/GO (b) XRD spectra of pristine (b) and (c) GP doped MOF.

The observed peaks at 9.5°, 16.6°, 25.8°, and 28.3° indicate successful incorporation of GO into the MOF structure. Notably, the peak at 9.5° is characteristic of GO, matching the standard reference JCPDS card No. 01-089-8967, thus confirming the presence of GO in the composite [7]. The optical band gap of the material was also proved by UV-visible spectroscopy proving the responsiveness to the visible light range. The property helps to conduct a photocatalytic activity at visible light irradiation efficiently. In water-based systems, photocatalysts activated by visible light have shown a great deal of promise for breaking down organic dyes. When compared to MOF, the MOF@GO hybrid catalyst exhibits a notable impact and excellent efficiency. UV-vis spectrometer is used to investigate the MOF@GO hybrid composite's photocatalytic activity. A mercury lamp was used to test the catalyst in the degradation reaction of an aqueous solution of methyl blue dye, with a glass screen removing UV-visible light wavelengths of 465 nm. The maximal absorbance of MB dye was used to examine the filtrate samples. (**Fig. S1**) explain the process of photocatalytic activity in which semiconductor theory is used to study photocatalytic activity for MB dye degradation.

In Fig. 3, the removal efficiency of MOF and MOF@GO MB dye were measured at different concentartion. The results indicates that MB dye concetrationis 2.5 mg/l, the romoval efficeny of MOF and MOF@GO, in which MOF@GO efficiency is high as compared to MOF. In-MOF@GO retained over 80% removal efficiency. These findings highlight the crucial role of GO in enhancing the adsorption capacity, particularly under higher pollutant loads. Therefore, In-MOF@GO appears to be a promising candidate for effective wastewater treatment. In photo-catalytic study MOFs and MOFs with doped GO prepared via solvothermal method exhibit good performance in degradation reaction of dye.

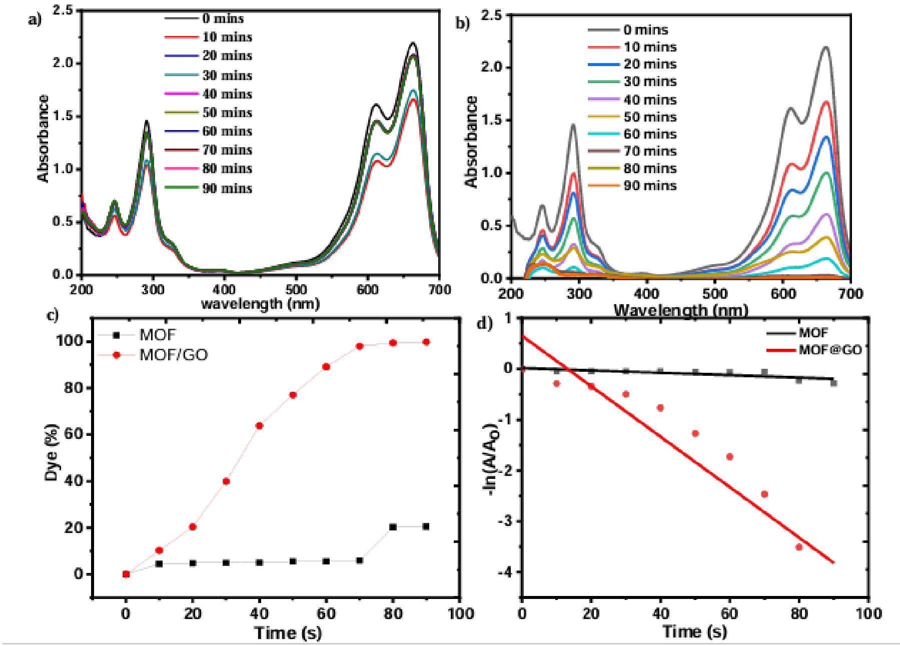

Figure 3: UV-Spectra of Absorption of MB Dye (A) Mofs And (B) MOF/GO Degradation Curves of Different Samples. (C) Dye Degradation Spectra of MOF And MOF/GO Experimental Data (B) Kinetic Analysis of MB Dye Degradation.

Fig 3.(a) and (b)show at 0 min the absorption of dye is more, but during time the absorbance of dye was decreased after a fix interval of time. In which MB dye absorbance decreased as a function of UV-Vis. radiation exposure time for different doped and undoped structure. It is observed from plots that MB dye concentration decreased with increasing UV-vis exposure time for all samples. The dye concentration decomposed by photo-catalytic experiment. It can be clearly seen within MOF@GO, increse in the surface area enhance the electron aceptor and provide more active site which helps the MB dye concentration decomposed at the end of the photocatalytic experiment. Fig 3(c) repersent the degradation of MB dye concentration variation for MOFs and MOFs/GO. It can be seen that MOFs/GO show good photocatalyst as compared to other samples. MOFs degradation is less than as compared to GO doped MOFs. The addition of graphene oxide (GO) into the MOF framework led to a drastic change in the dye degradation efficiency, up to 99 %. The kinetic behaviour which as shown in Fig. 3(d) [8]. The calculated values of MOF and MOF@GO hydrid structure were 2.83 and $4.96x10^{-2}$.

Conclusion

In conclusion, we have reported MOF@GO hybrid materials prepared by the solvo-thermal method for MB dye degradation. This material showed enhanced photo-catalytic efficiency as compared to MOF material for MB dye degradation under visible light irradiation. The MOF@GO hybrid structure improved the photo degradation properties. This composite shows high degradation efficiency (99%) as compared to MOF, which is 21%. Furthermore, its kinetic rate constant is also 4.96×10^{-2}. In addition, MOF@GO is not only suitable candidate to improve the environment pollution but also beneficial for the waste--to-wealth approach.

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