ADSORPTION AND PHOTOCATALYTIC REMOVAL OF METHYLENE BLUE USING GRAPHENE OXIDE-SUPPORTED ENGELHARD TITANOSILICATE-10

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FACULTY OF SCIENCE AND NATURAL RESOURCES
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IJAZAH: **MASTER OF SCIENCE (INDUSTRIAL CHEMISTRY)**

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DECLARATION

I hereby declare that the material in this thesis is my own except for quotations, excerpts, equations, summaries and references, which have been duly acknowledged.

7th July 2017

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ABSTRACT

In this study, ETS-10 precursors were mixed with graphene oxide (GO) suspension to obtain GO incorporated ETS-10 (GO/ETS-10) with improved adsorption ability and photocatalytic activity in comparison to that of ETS-10. The GO/ETS-10 composite prepared with different GO to ETS-10 ratios, *i.e.* 1:15, 1:10 and 1:5 were confirmed by XRD, FTIR, EDX and XPS analyses. The results showed that GO and ETS-10 were chemically bound through Ti–O–C and Si–O–C bonding. SEM images showed that the truncated bipyramidal ETS-10 crystals were grown firmly on the GO surface and have crystal sizes range between 0.5 to 1.0 μm. Thermogravimetric analysis revealed that the synthesized GO/ETS-10 composite was thermally stable up to 150 ˚C and decomposed fully above 400 ˚C due to the disintegration of GO from ETS-10. The band gap energy for GO/ETS-10(1:5) was determined to be 3.12 eV which was lower than ETS-10 (3.48 eV). The adsorption study revealed that the adsorption behavior of MB onto GO/ETS-10 was mainly monolayer due to the chemisorption interaction between MB and GO/ETS-10 surface. The maximum equilibrium adsorption capacity of GO/ETS-10 was calculated to be 294 mg/g, which is much higher than ETS-10 with only 139 mg/g. Besides that, GO/ETS-10 can be photoexcited by both UV-A and visible radiations which gave similar removal of MB in water. This implies that the presence of GO can help to widen the light responsive range of ETS-10 by lowering the band gap energy and suppress the electron-hole recombination. 0.075 g/L of GO/ETS-10(1:5) in 20-ppm MB solution with UV-A irradiation (as GO/ETS-10(1:5)/UV-A), for instance, can achieve about 65 % of MB removal after 6 hours and still increasing with a consistent rate of removal in comparison to 60 % of MB removal achieved by GO/ETS-10(1:5)/Dark system, which has reached plateau after 6 hours of reaction. The results showed that the photocatalytic activity of GO/ETS-10 was low under UV-A irradiation but it is important to ensure continuous adsorption-photocatalytic removal throughout the process. Besides, it was found that addition of 5 x 10^{-3} mol/L H_2O_2 in the photocatalytic system (as GO/ETS-10(1:5)/H_2O_2/UV-A system) was capable to enhance about 20 % of MB removal, which giving a total of 93 % after 8 hours. This study implies that GO/ETS-10 composite can be a potential material specifically for the elimination of organic pollutant via adsorption and eventually through photocatalytic decomposition under sunlight.

ABSTRAK

PENJERAPAN DAN FOTO-PEMANGKINAN METILENA BIRU MENGGUNAKAN ENGELHARD TITANOSILICATE-10 BERGANDING GRAFENA OKSIDA

Dalam kajian ini, pelopor ETS-10 telah dicampur dengan larutan grafena oksida (GO) untuk mendapatkan bahan ETS-10 terganding GO (GO/ETS-10) yang mempunyai keupayaan penjerapan dan aktiviti foto-pemangkinan yang baik berbanding dengan ETS-10. Komposit GO/ETS-10 yang telah disediakan dalam tiga nisbah GO terhadap ETS-10 yang berbeza, iaitu 1:15, 1:10 dan 1:5 telah dicirikan menggunakan XRD, FTIR, EDX dan analisis XPS. Hasil kajian menunjukkan bahawa GO dan ETS-10 adalah terikat melalui ikatan kimia antara Ti-O-C dan Si-O-C. Imej SEM menunjukkan bahawa hablur bipiramid ETS-10 telah bertumbuh dengan teguh di atas permukaan GO dan mempunyai saiz hablur antara 0.5 hingga 1.0 µm. Analisis termogravimetri mendedahkan bahawa komposit GO/ETS-10 yang disediakan mempunyai kestabilan haba sehingga 150 °C dan ia terurai sepenuhnya selepas 400 °C akibat pemisahan GO dari ETS-10. Jurang tenaga untuk GO/ETS-10(1:5) yang diujikan adalah 3.12 eV dan ia lebih rendah berbanding dengan ETS-10 (3.48 eV). Kajian penjerapan menunjukkan bahawa penjerapan MB ke atas permukaan GO/ETS-10 merupakan lapisan tunggal akibat penjerapan kimia antara MB dan permukaan GO/ETS-10. Kapasiti penjerapan maksimum GO/ETS-10 secara pengiraan adalah 294 mg/g, dan ia adalah 2 kali lebih tinggi berbanding dengan ETS-10 yang hanya mencapai 139 mg/g. Selain itu, juga didapati aktiviti foto-pemangkinan GO/ETS-10 boleh diaktifkan oleh kedua-dua UV-A dan sinaran cahaya nampak dan memberikan penyingkiran MB yang lebih kurang sama dalam air. Ini menunjukkan bahawa kehadiran GO dapat membantu memperluaskan julat responsif cahaya ETS-10 dengan mengurangkan jurang tenaga dan menyekat penggabungan semula elektron-lohong. 0.075 g/L GO/ETS-10(1:5) dalam 20 ppm larutan MB di bawah sinaran UV-A (sebagai GO/ETS-10(1:5)/UV-A), contohnya, boleh menyingkirkan sebanyak 65 % terhadap MB selepas 6 jam dan masih berterusan dengan kadar penyingkiran yang positif berbanding dengan hanya 60 % MB diingkirkan oleh GO/ETS-10(1:5)/gelap, yang telah mencapai keseimbangan selepas 6 jam tindak balas. Hasil kajian menunjukkan bahawa aktiviti foto-pemangkinan GO/ETS-10 adalah rendah di bawah sinaran UV-A tetapi ia amat penting untuk memastikan penyingkiran MB secara penjerapan dan foto-pemangkinan berterusan sepanjang masa. Selain itu, penambahan 5 x 10^{-3} mol/L H_2O_2 dalam sistem foto-pemangkinan (sebagai sistem GO/ETS-10(1:5)/H_2O_2/UV-A) mampu meningkatkan sebanyak 20 % penyingkiran MB, dan memberikan 93 % penyingkiran keseluruhan MB selepas 8 jam. Kajian ini menunjukkan bahawa komposit GO/ETS-10 boleh menjadi satu bahan yang berpotensi untuk penyingkiran bahan pencemar organik melalui penjerapan dan akhirnya terurai melalui foto-pemangkinan di bawah sinaran cahaya matahari.

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LIST OF SYMBOLS AND ABBREVIATIONS

Abs	-	Absorbance
EDX	-	Energy-dispersive X-ray
ETS	-	Engelhard Titanosilicate
eV	-	Electronvolt
e^-	-	Electron
FTIR	-	Fourier transform infrared spectroscopy
GO	-	Graphene oxide
h^+	-	Photogenerated holes
HOPG	-	Highly-ordered pyrolytic graphite
MB	-	Methylene Blue
MOFs	-	Metal-organic framework
SEM	-	Scanning electron microscopy
TGA	-	Thermogravimetric analyzer
UV-A	-	Ultraviolet A
UV-Vis	-	Ultraviolet-visible
XRD	-	X-ray diffractometer
wt %	-	Weight percentage
•OH	-	Hydroxyl radical
$•O^{2-}$	-	Superoxide radical
λ_{max}	-	Maximum wavelength
π	-	pi bond
π^*	-	Anti-bonding pi
σ	-	Sigma bond

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