



#### ISSN: 2576-8840



\*Corresponding author: Yousheng Tao, College of Materials Science and Engineering, Sichuan University, Chengdu 610065, China

**Submission:** i July 21, 2023 **Published:** August 07, 2023

Volume 19 - Issue 2

How to cite this article: Nady Fathy and Yousheng Tao\*. Synergistic Effect of Nanocarbons and their Supported Single/ Binary Transition Metal Oxides on Dye Removal. Res Dev Material Sci. 19(2). RDMS. 000959. 2023. DOI: 10.31031/RDMS.2023.19.000959

**Copyright@** Yousheng Tao, This article is distributed under the terms of the Creative Commons Attribution 4.0 International License, which permits unrestricted use and redistribution provided that the original author and source are credited.

# Synergistic Effect of Nanocarbons and their Supported Single/Binary Transition Metal Oxides on Dye Removal

### Nady Fathy<sup>1</sup> and Yousheng Tao<sup>2\*</sup>

<sup>1</sup>Physical Chemistry Department, National Research Centre, Egypt <sup>2</sup>College of Materials Science and Engineering, Sichuan University, China

#### Abstract

Nanocarbons such as nanopore-structured carbon, carbon nanotubes and graphene have inherently excellent conductivity, large specific surface area, and chemical and mechanical stability. The combination of single/binary transition metal oxides with nanocarbon materials provides synergistic effect on their applications such as in environment and energy aspects, superior to the individual component alone. This article briefly described the enhanced performance of the dye removal with nanocarbons and their supported single/binary transition metal oxides in recent literature.

### Introduction

A significant volume of printing and dyeing effluent has been generating worldwide. The amount of discharged textile dye wastewater accounts for high percentage of total wastewater discharge, posing a serious danger to environmental security [1,2]. Additionally, the dyes are non-biodegradable, mutagenic and carcinogenic effects to humans. As a result, establishing modern and cost-effective techniques to meet stated criteria for remediating water and wastewater, as well as population needs, is now a requirement. Among developed methods, many researchers focused on the adsorption using metal oxide supported in single or binary form on different carbon materials as a promising method to overcome the previous shortcomings of adsorption by activated carbon (AC) alone, for example [3,4]. Accordingly, the combination of metal oxides with carbon materials can enhance the adsorption of dyes with further degradation operations according to type of these oxides including advanced oxidation processes (e.g., Fenton-oxidation, photo-oxidation as exposed to light source and wet oxidation with  $H_2O_2$  [3-7]. Thus, a synergistic effect is obtained due to the presence of single/binary transition metal oxides (S/BTMOs) supported on carbon materials. Among them, binary transition metal oxides with spinel structures such as CuMn<sub>2</sub>O<sub>4</sub>, MnCo<sub>2</sub>O<sub>4</sub>, ZnMn<sub>2</sub>O<sub>4</sub>, NiMn<sub>2</sub>O<sub>4</sub>, CuCo<sub>2</sub>O<sub>4</sub>, MnFe<sub>2</sub>O<sub>4</sub>, and Mn<sub>2</sub>CuO<sub>4</sub> have recently become an importance in industrial, environmental and energy applications [8-13].

### Activated carbons and their supported single/binary transition metal oxides (S/BTMOs) for enhanced dye removal

In recent years, the loaded magnetic metal oxides on the AC gained much interest in order to improve the adsorption capacity and make the possible recovery of powdered adsorbents [3,4]. For example, some studies have prepared magnetic oxides in single/binary states using especially iron oxide for developing a magnetized activated carbon by simple economic separation. The adsorption and recovery by magnetic separation of AC loaded by  $Fe_2O_3$  [14], Au-Fe\_3O\_4 [15], and NiFe\_2O\_4 [16] have greatly improved. Other oxides such as cerium dioxide  $(CeO_2)$ , zinc oxide (ZnO) [17], manganese dioxide  $(MnO_2)$  [18] titanium oxide  $(TiO_2)$  [19] and Ce-TiO\_2 [20] have been supported on AC to increase the catalytic degradation of dyes. These oxides loaded on AC can increase the convenience of operation, recovery, and efficiency of adsorption processes as a result of a synergistic effect.

### Carbon nanotubes and their supported S/BTMOs for enhanced dye removal

Carbonaceous nanostructures are a deterministic support in water treatment because of their functional properties such as large surface area, high mechanical strength, high porosity, a significant aspect ratio, strong thermal and electrical properties, good chemical stability, impressive hydrophobicity, simplicity of use, and separation characteristics [21,22]. In particular, magnetic oxides loaded on carbon nanotubes (CNTs) hold remarkable properties such as surface-volume ratio, higher surface area and convenient separation methods to be effective adsorbents in removal of heavy metals and dye [23]. Recently, the synthesis of manganese dioxide (MnO<sub>2</sub>) loaded on multi-walled carbon nanotubes (MWCNTs) has attracted tremendous increasing research interest in dye removal via Fenton-reaction degradation [24,25]. The combination of both adsorption process and catalytic oxidation processes through MnO<sub>2</sub>/MWCNTs nanocomposite system could be provided a simple, efficiently and environmentally friendly water treatment. Photodegradation of methylene blue dye enhanced significantly over fabricated CNTs-supported Mn-TiO<sub>2</sub> [5], CNTs/TiO<sub>2</sub>/AgNPs/ surfactant nanocomposites [7], as well as Fenton-catalyst based Cu<sub>2</sub>S-TiO<sub>2</sub>/MWCNTs nanocomposites [6]. NiO and Co<sub>2</sub>O<sub>3</sub>, NiCo<sub>2</sub>O<sub>4</sub>, and NiCo<sub>2</sub>O<sub>4</sub>/MWCNTs nanocomposites have been synthesized and studied for photodegradation of Reactive Red 120 dye [26], where NiCo<sub>2</sub>O<sub>4</sub>/MWCNTs enhanced largely the photodegradation.

## Graphenes and their supported S/BTMOs for enhanced dye removal

Graphene has emerged as a useful nano-adsorbent for environmental applications because of its high theoretical specific surface area (~2630m<sup>2</sup>g<sup>-1</sup>) [27]. Moreover, abundant oxygencontaining functional groups have been incorporated in graphene to get graphene oxide (GO) and reduced graphene oxide (RGO) to enhance their adsorption capability [28,29]. Maximum adsorption capacities of methylene blue dye on the MFe<sub>2</sub>O<sub>4</sub>@GO (M=Cu, Co or Ni) were 25.81, 50.15 and 76.34mg g<sup>-1</sup>, respectively [30]. Hsieh et al. reported degradation of acid orange 7 (AO7) by Pt-TiO<sub>2</sub>/G nanocomposites [31]. Pt-TiO<sub>2</sub> can be served as a chargegenerating centre while graphene acted as an electron acceptor and transporter in the composite. Ultra large surface area and strong  $\pi$ - $\pi$  interaction on the surface of graphene - based metal oxides are responsible for adsorption [28].

### Conclusion

Nanocarbons such as nanopore-structured carbon, carbon nanotubes (CNTs) and graphene can be used as substrates for the loading of single/binary transition metal oxides to make nanocompostes. The combination of metal oxides with nanocarbon materials gives synergistic effect on dye removal. The nanocomposites showed enhanced adsorption of dyes with further degradation processes according to type of these oxides, including advanced oxidation processes as reported in literature as Fenton-oxidation, photo-oxidation as exposed to light source and wet oxidation with  $H_2O_2$ . Among them, binary transition metal oxides with spinel structures such as  $CuMn_2O_4$ ,  $MnCo_2O_4$ ,  $ZnMn_2O_4$ ,  $NiMn_2O_4$ ,  $CuCo_2O_4$ ,  $MnFe_2O_4$ , and  $Mn_2CuO_4$  loaded on nanocarbons have recently become an importance in industrial, environmental and energy applications.

### Acknowledgement

This work was supported by the Fundamental Research Funds for the Central Universities, China (20822041E4065,20826041F4087), Sichuan University-Yibin Municipal Government Cooperation Project (2020CDYB-33), and Sichuan Provincial Government in China (0082204151556).

### **Conflict of Interest**

The authors declare no conflict of interest.

#### References

- 1. Mia R, Selim M, Shamim AM, Chowdhury M, Sultana S, et al. (2019) Review on various types of pollution problem in textile dyeing & printing industries of Bangladesh and recommendation for mitigation. J Text Eng Fash Technol 5: 220-226.
- Li J, Han L, Zhang T, Qu C, Yu T, et al. (2022) Removal of methylene blue by metal oxides supported by oily sludge pyrolysis residues. Appl Sci 12: 4725.
- Bichave MS, Kature AY, Koranne SV, Shinde RS, Gongle AS, et al. (2023) Nano-metal oxides-activated carbons for dyes removal: A review. Materials Today: Proceedings 77(1): 19-30.
- Nayeri D, Mousavi SA (2020) Dye removal from water and wastewater by nanosized metal oxides -modified activated carbon: a review on recent researches. J Environm Health Sci Eng 18: 1671-1689.
- 5. Zhang M, Gao J, Chen T, Annamalai KP, Tao Y (2018) Synthesis of carbon nanotube-supported  $Mn-TiO_2$  as a photocatalyst under visible light. Rec Innov Chem Eng 11(1): 45-49.
- Zhang M, Annamalai KP, Chen T, Tao Y (2018) Synthesis of Cu<sub>2</sub>S-TiO<sub>2</sub>/ MWCNTs nanocomposites for photo- fenton-like reaction. Rec Innov Chem Eng 11(1): 15-19.
- Azzam EMS, Fathy NA, El-Khouly SM, Sami RM (2019) Enhancement the photocatalytic degradation of methylene blue dye using fabricated CNTs/TiO<sub>2</sub>/AgNPs/Surfactant nanocomposites. J Water Proc Eng 28: 311-321.
- 8. Gao Y, Li B, Zhang Z, Zhang X, Deng Z, et al. (2021)  $CuMn_2O_4$  spinel nanoflakes for amperometric detection of hydrogen peroxide. ACS Appl Nano Mater 4(7): 6832-6843.
- Li L, Jiang G, Ma J (2018) CuMn<sub>2</sub>O<sub>4</sub>/graphene nanosheets as excellent anode for lithium-ion battery. Materials Research Bulletin 104: 53-59.
- 10. Bhowmick S, Moi CT, Kalita N, Sahu A, Suman S, et al. (2021) Spontaneous fenton-like dye degradation in clustered-petal di-manganese copper oxide by virtue of self-cyclic redox couple. J Environmental Chemical Engineering 9: 106094.
- 11. Sobhani A (2022) Hydrothermal synthesis of  $\text{CuMn}_2\text{O}_4/\text{CuO}$  nanocomposite without capping agent and study its photocatalytic activity for elimination of dye pollution. International J Hydrogen Energy 47(46): 20138-20152.

- 12. Kazemi MS, Sobhani A (2023)  $CuMn_2O_4/chitosan micro/nanocomposite: Green synthesis, methylene blue removal, and study of kinetic adsorption, adsorption isotherm experiments, mechanism and adsorbent capacity. Arabian J Chem 16 (6): 104754.$
- 13. Chen X, Chen T, Fathy N, Tao Y (2023) Preparation of carbon nanotubessupported nanocomposites for highly efficient degradation of methylene blue dye. Rec Innov Chem Eng 16 (in press).
- 14. Reza RA, Ahmaruzzaman M (2015) A novel synthesis of  $Fe_2O_3@$ activated carbon composite and its exploitation for the elimination of carcinogenic textile dye from an aqueous phase. RSC Adv 5(14): 10575-10586.
- 15. Bagheri S, Aghaei H, Monajjemi M, Ghaedi M, Zare K (2018) Novel Au-Fe<sub>3</sub>O<sub>4</sub> NPs loaded on activated carbon as a green and high efficient adsorbent for removal of dyes from aqueous solutions: application of ultrasound wave and optimization. Eurasian J Analytical Chem 13(3): 23.
- 16. Livani MJ, Ghorbani M (2018) Fabrication of NiFe<sub>2</sub>O<sub>4</sub> magnetic nanoparticles loaded on activated carbon as novel nanoadsorbent for direct red 31 and direct blue 78 adsorption. Environ Technol 39(23): 2977-2993.
- 17. Sahar M El-Khouly, Ghada M Mohamed, Nady A Fathy, Gehan A Fagal (2017) Effect of nanosized CeO<sub>2</sub> or ZnO loading on adsorption and catalytic properties of activated carbon. Adsorp Sci Technol 35: 774-788.
- 18. Pargoletti E, Pifferi V, Falciola L, Facchinetti G, Depaolini AR, et al. (2019) A detailed investigation of MnO<sub>2</sub> nanorods to be grown onto activated carbon. High efficiency towards aqueous methyl orange adsorption/ degradation. Appl Surf Sci 472: 118-126.
- 19. Tarek S Jamil, Montaser Y Ghaly, Nady A Fathy, Tarek A Abd El-Halim, Lars Österlund (2021) Enhancement of TiO<sub>2</sub> behavior on photocatalytic oxidation of MO dye using TiO<sub>2</sub>/AC under visible irradiation and sunlight radiation. Sep Purif Techenol 98: 270-279.
- 20. Dil EA, Ghaedi M, Asfaram A, Mehrabi F, Bazrafshan AA, et al. (2019) Synthesis and application of Ce-doped  $\text{TiO}_2$  nanoparticles loaded on activated carbon for ultrasound-assisted adsorption of basic red 46 dye. Ultrason Sonochem 58: 104702.
- 21. Mittal G, Dhand V, Rhee KY, Park SJ, Lee WR (2015) A review on carbon nanotubes and graphene as fillers in reinforced polymer nanocomposites. J Indust Eng Chem 21: 11-25.

- 22. Xu J, Cao Z, Zhang Y, Yuan Z, Lou Z, et al. (2018) A review of functionalized carbon nanotubes and graphene for heavy metal adsorption from water: Preparation, application, and mechanism. Chemosphere 195: 351-364.
- 23. Khan FSA, Mubarak NM, Tan YH, Khalid M, Karri RR, et al. (2021) A comprehensive review on magnetic carbon nanotubes and carbon nanotube-based buckypaper for removal of heavy metals and dyes. Journal of Hazardous Materials 413: 125375.
- 24. Fathy NA, El-Shafey SE, El-Shafey OI, Mohamed WS (2013) Oxidative degradation of RB19 dye by a novel γ–MnO<sub>2</sub>/ MWCNT nanocomposite catalyst with H<sub>2</sub>O<sub>3</sub>. J Environ Chem Eng 1: 858-864.
- 25. Fathy NA, El-Shafey SE, El-Shafey OI (2017) Synthesis of a novel MnO<sub>2</sub>@ carbon nanotubes-graphene hybrid catalyst (MnO<sub>2</sub>@CNT-G) for catalytic oxidation of basic red 18 dye (BR18). J Water Proc Eng 17: 95-101.
- 26. Shokrgozar A, Seifpanahi-Shabani K, Mahmoodi B, Mahmoodi NM, Khorasheh F, et al. (2021) Synthesis of Ni-Co-CNT nanocomposite and evaluation of its photocatalytic dye (Reactive Red 120) degradation ability using response surface methodology. Desalination and Water Treatment 216: 389-400.
- 27. Shahadat M, Momina A, Ismail S, Faraz M, Ansari MZ, et al. (2019) Graphene-metal oxide-supported nanohybrid materials for treatment of textile dyes. Mohammad J, Akil A, David L (Eds.), in micro and nano technologies. Graphene-Based Nanotechnologies for Energy and Environmental Applications, pp. 315-328.
- Khurana I, Saxena A, Bharti, Khurana JM, Rai PK (2017) Removal of dyes using graphene-based composites: A review. Water Air Soil Pollut 228: 180.
- 29. El-Khouly SM, Fathy NA, Farag HK, Aboelenin RMM (2020)  $In_2O_3$  catalyst supported on carbonaceous nanohybrid for enhancing the removal of methyl orange dye from aqueous solutions. Des Water Treat 174: 344-353.
- 30. Bayantong ARB, Shih YJ, Ong DC, Abarca RRM, Dong CD, et al. (2021) Adsorptive removal of dye in wastewater by metal ferrite-enabled graphene oxide nanocomposites. Chemosphere 274: 129518.
- Hsieh SH, Chen WJ, Wu CT (2015) Pt-TiO<sub>2</sub>/graphene photocatalysts for degradation of AO7 dye under visible light. Applied Surface Science 340: 9-17.