Preparation and Characterization of SnO$_2$/AC as a Novel High Surface Area Nanocatalyst

Abdul Rahman Y. Wahoud$^{1*}$, Salim F. Bamsaoud$^1$, Mohammed A. Al-Haiqi$^1$

$^1$ Chemistry Department, College of Science, Hadhramout University, P. O. B. 50511, Mukalla, Yemen
$^*$ Corresponding author, e-mail: awahoud8@gmail.com

Received: 06 June 2020, Accepted: 29 July 2020, Published online: 10 May 2021

Abstract
A new solid nanoparticle sorbent (SnO$_2$/AC) could serve as high surface area and inexpensive nanocatalyst was prepared. Many properties were characterized by SEM and UV spectroscopy. High surface area, large micro pore volume and total pore volume were found to be 571 m$^2$ g$^{-1}$, 0.4785 cm$^3$ g$^{-1}$ and 0.7267 cm$^3$ g$^{-1}$ respectively even with very high loaded ratio (60 %) of tin dioxide to Activated Carbon (SnO$_2$/AC). Taguchi factorial design method was used to get the maximum MB dye adsorption on the surface of SnO$_2$/AC nanoparticle sorbent. Contact time (60 min), initial dye concentration (5 mM) and solution temperature (293 K) were found to be the best conditions for the more effective absorption process.

Keywords
nanocatalyst, Taguchi method, tin dioxide, Activated Carbon (AC)

1 Introduction
The most extensive work has been performed on the metals and their oxides supported on active carbon instead of SiO$_2$–Al$_2$O$_3$ [1–5]. They are considered to be as most promising catalysts because they are friendly environment and more active and selective, especially nanoparticles catalysts which have high surface area and large micro pore volume [6–8]. Various kinds of precursors have been modified with different materials and methods to produce high surface Activated Carbon (AC) such as peanut hulls [9], coconut husk [10], rice husk [11], bamboo [12], fruit stone [13] and papaya leaves [14]. Among of these agricultural wastes, Date Stones (DS) considered as the best candidate because it is cheap and abundantly available [15]. Moreover it has high surface area and it is easy to treated and activated [16, 17]. Taguchi statistical method was utilized in order to find out the ideal parameters for effective and maximum adsorption capacity of Methylene Blue (MB) dye with low cost of experiments and less time consuming [18, 19]. In this study we have prepared and characterized SnO$_2$/AC nanocatalyst and find out the ideal conditions for MB adsorption process by using statistical method. In addition to study and evaluate the adsorption performance of SnO$_2$/AC for the removal of MB from aqueous solutions to avoid environmental pollution.

2 Materials and methods
2.1 Materials
SnCl$_2$·2H$_2$O, CH$_3$COOH, H$_2$SO$_4$, KOH, Acetone, Ethanol and Methylene Blue (MB) dye and all chemicals reagents in analytical grad were used from Uni-Chem.

Fig. 1 shows the MB dye structure (molecular formula C$_{16}$H$_{18}$N$_3$SCl, 3H$_2$O, $\lambda_{\text{max}}$ of 665 nm, $M_w = 373.9$ g mol$^{-1}$). It is recognized usefulness in characterizing adsorptive material and used as a model to remove colored contaminants from aqueous solutions.

2.2 Date Stone activation
Yemeni Date Stones (DS) washed several times with distilled water, dried, crushed and sieved with average particle size of 250 μm. Powder were soaked in 30 % KOH at room temperature with 1:20 weight ratio (DS: KOH) for 24 hour.

![Fig. 1 Methylene Blue (MB) structure](image-url)
the solution was shake from time to another. Then potassium hydroxide solution was decanted and impregnated sample was put crucible with lid and carbonized by heated up to 648 K in muffle furnace for 2 hour. Then the sample was cooled and washed with of 0.01 M H₂SO₄ until the filtrate neutralization. After that, the Activated Carbon filtrated and dried at 378 K for 3 hours [17]. Table 1 shows the properties of raw Date Stone and Activated Carbon.

### 2.3 Preparation of SnO₂/AC nanocatalyst

SnO₂/AC nanocatalyst was prepared by precipitation of Sn(II) ions at Activated Carbon (AC), which we obtained from the Date Stones (DS), in aqueous solution. First, 2 g stannous chloride dissolved in 8 cm³ of distilled water. Then 4 ml of glacial acetic acid was added into SnCl₂ solution and stirred for 1 h at 343 K. Then the solution was put in the oven at 673 K for 1.5 h to decompose all SnCl₂ and converted Sn II to SnO₂ nanoparticles [20]. After that a certain amounts of Activated Carbon and SnO₂ nanoparticles added to 25 cm³ of distilled water and stirred continuously and heated until most of water evaporated. Then the sample was entered the oven for 2 h at 403 K. The SnO₂/AC nanocatalyst powder kept labeled in sealed glass flask for used in following experiments. The simple explanation of the mechanism of formation and growth of SnO₂ in the presence of Activated Carbon can be described by the following by the following [20, 21]:

\[
\text{SnCl}_2 \xrightarrow{\text{Aqueous solution}} \text{Sn}^{2+} + 2\text{Cl}^{-} \\
\text{Sn}^{2+} + \text{CH}_3\text{COOH} \xrightarrow{\text{Aqueous solution}} \left(\text{CH}_3\text{COO}\right)_2\text{Sn} + 2\text{H}^+ \\
\left(\text{CH}_3\text{COO}\right)_2\text{Sn} \xrightarrow{\text{Glycolic acid, 40°C}} \text{SnO}_2 + \text{CO}_2 + \text{CO} \\
\text{SnO}_2 + \text{AC} \xrightarrow{\text{Aqueous solution}} \text{SnO}_2(\text{AC})_{(aq)} \\
\text{SnO}_2(\text{AC})_{(aq)} \xrightarrow{\text{Heat Treatment}} \text{SnO}_2(\text{AC})_{(s)}.
\]

### 2.4 Surface area and pore structure calculation

The surface area, micro pore volume (\(V'_m\)) and total pore volume (\(V'_t\)) of the samples were estimated by the following models [22]:

\[
S(\text{cm}^2 \text{ g}^{-1}) = 2.28 \times 10^2 - 1.01 \times 10^1 \text{MBN} + 3.00 \times 10^1 \text{IN} + 1.05 \times 10^4 \text{MBN}^2 + 2.00 \times 10^4 \text{IN}^2 + 9.38 \times 10^4 \text{MBN} \times \text{IN} \tag{1}
\]

\[
V'_m(\text{cm}^3 \text{ g}^{-1}) = 5.60 \times 10^{-2} - 1.00 \times 10^{-3} \text{MBN} + 1.55 \times 10^{-4} \text{IN} + 7.00 \times 10^{-6} \text{MBN}^2 + 1.00 \times 10^{-7} \text{IN}^2 - 1.18 \times 10^{-7} \text{MBN} \times \text{IN} \tag{2}
\]

\[
V'_t(\text{cm}^3 \text{ g}^{-1}) = 1.37 \times 10^{-1} + 1.9 \times 10^{-3} \text{MBN} + 1 \times 10^{-4} \text{IN}, \tag{3}
\]

where (IN) is Iodine Number and (MBN) is Methylene Blue Number.

### 2.5 Taguchi statistical method

The orthogonal array are used to conduct a set of experiments [18, 19], and \(S/N\) ratio are employed to study the performance characteristics of MB adsorption onto the prepared SnO₂/AC nanocatalyst. Four factors with three levels were designed in as shown in Table 2. A standard \(L_{27}\) array was used to determine the ideal conditions for maximum MB dye adsorption. The experimental results were shown in Table 3. The larger (\(S/N\)) ratio was selected to be the better. The \(S/N\) ratio was defined as [18]:

\[
\frac{S}{N} = 10 \log \left(\frac{1}{Y_1^2 + 1/Y_2^2 + \ldots + 1/Y_n^2}\right),
\]

where \(n\) the number of replicates and \(y\) is the experimental value.

### 2.6 Determination of Adsorption Capacity

To determine of adsorption capacity, 50 cm³ of varying concentrations of MB dye were contacted with 0.5 g of every absorbent placed in 250 cm³ conical flask. The conical flask were tightly covered. The sample was putted
at room temperature (298 ± 2 K) on a magnetic stirrer with a thermostat to control the temperature, to reach equilibrium. All experiments were performed at 555 rpm.

Then the samples were filtered and analyzed by an ultraviolet Spectrophotometer (Jasco V-730) at $\lambda_{\text{max}}$ 665 nm. The uptake of MB dye adsorbed $q_t$ on SnO$_2$/AC surface was calculated as following:

$$q_t = \frac{(C_0 - C_t)}{W} \times V,$$

where $C_0$ and $C_t$ (mg dm$^{-3}$) are the initial and equilibrium of MB dye concentrations respectively, $V$ (dm$^3$) is the solution volume and $W$ (g) is the weight of Date Stone.

### Results and discussion

#### 3.1 SnO$_2$/AC characterizations

Fig. 2 shows the ultraviolet spectrum for SnO$_2$ solution, it has an absorption peak at 295 nm which corresponds to band gap energy of ~4.2 eV, which indicates nanoparticle size comparable to that of the bulk Bohr exciton radius found to be ~2.7 nm [20, 23]. The XRD data for SnO$_2$ nanoparticle (Fig. 3) shows that all the peaks are related to SnO$_2$ tetragonal phase which were confirmed with the standard JCPDS data (No. 72-1147). No other peaks were present related to any phase of SnO$_2$. The peaks 26.6, 33.7 and 51.7° were considered to calculate the average crystallite size using Scherer formula and the crystallite size was found to be 8 nm. In agreement with XRD data the TEM and SEM for SnO$_2$ nanoparticle (Figs. 4, 5) shows that the size was about 8 nm. The Scanning Electron Microscope (SEM) of the SnO$_2$/AC surface (Fig. 6) clearly indicates that the nanostructures of SnO$_2$/AC which we obtained and shows a good scattering of SnO$_2$ inside the pores of Activated Carbon and no SnO$_2$ crystallites were found out of the pores.
3.2 Mechanism of control of SnO$_2$/AC nanocatalyst formation

The effect of reaction conditions in the synthesis of SnO$_2$/AC on the surface area and pore volume of nanocatalyst (Fig. 6) was studied by loading different mass present ratios of tin dioxide to Activated Carbon SnO$_2$/AC (0, 10, 20, 40, 60, 100 wt%) according to the experimental procedures. The result was put in the Table 3. It clear that, although the surface area and pore volume decrease by increasing the SnO$_2$/AC ratio, but they haven't affected so much and the SnO$_2$/AC 60 % nanocatalyst still have a high surface area 571 cm$^2$ g$^{-1}$ with large micropores volume 0.4785 cm$^3$ g$^{-1}$ and large total pores volume 0.7267 cm$^3$ g$^{-1}$, this indicates that the nanoparticles of tin dioxide don’t agglomerate and don’t blog the pores. They don’t crystalline outside of the pores.

3.3 Effects of parameters on the adsorption process

To study the effects of parameters on the MB dye adsorption onto SnO$_2$/AC nanocatalyst, Taguchi factorial design method was used. The results for each experiment were put in Table 4. The results show that the uptake of MB varied from 32.49 mg g$^{-1}$ to 237.96 mg g$^{-1}$, and S/N ratios

| Expt. No. | Contact time (min) | Initial conc. (mM) | SnO$_2$/AC ratio (%) | Temperature (K) | Uptake (mg g$^{-1}$) | S/N ratio |
|-----------|---------------------|--------------------|----------------------|-----------------|----------------------|-----------|
| 1         | 15                  | 1                  | 10                   | 293             | 40.23                | 32.09     |
| 2         | 15                  | 1                  | 10                   | 313             | 36.52                | 31.25     |
| 3         | 15                  | 1                  | 10                   | 333             | 32.49                | 30.23     |
| 4         | 15                  | 2.5                | 20                   | 293             | 73.47                | 37.32     |
| 5         | 15                  | 2.5                | 20                   | 313             | 70.77                | 36.99     |
| 6         | 15                  | 2.5                | 20                   | 333             | 67.83                | 36.62     |
| 7         | 15                  | 5                  | 40                   | 293             | 96.63                | 39.70     |
| 8         | 15                  | 5                  | 40                   | 313             | 94.11                | 39.47     |
| 9         | 15                  | 5                  | 40                   | 333             | 92.54                | 39.32     |
| 10        | 30                  | 1                  | 20                   | 293             | 57.92                | 35.25     |
| 11        | 30                  | 1                  | 20                   | 313             | 55.24                | 34.84     |
| 12        | 30                  | 1                  | 20                   | 333             | 53.22                | 34.52     |
| 13        | 30                  | 2.5                | 40                   | 293             | 141.91               | 43.04     |
| 14        | 30                  | 2.5                | 40                   | 313             | 137.77               | 42.78     |
| 15        | 30                  | 2.5                | 40                   | 333             | 135.43               | 42.63     |
| 16        | 30                  | 5                  | 10                   | 293             | 205.11               | 46.23     |
| 17        | 30                  | 5                  | 10                   | 313             | 203.12               | 46.15     |
| 18        | 30                  | 5                  | 10                   | 333             | 201.34               | 46.07     |
| 19        | 60                  | 1                  | 40                   | 293             | 60.07                | 35.57     |
| 20        | 60                  | 1                  | 40                   | 313             | 58.65                | 35.36     |
| 21        | 60                  | 1                  | 40                   | 333             | 56.34                | 35.01     |
| 22        | 60                  | 2.5                | 10                   | 293             | 155.76               | 43.84     |
| 23        | 60                  | 2.5                | 10                   | 313             | 153.73               | 43.73     |
| 24        | 60                  | 2.5                | 10                   | 333             | 151.88               | 43.63     |
| 25        | 60                  | 5                  | 20                   | 293             | 237.96               | 47.53     |
| 26        | 60                  | 5                  | 20                   | 313             | 233.71               | 47.37     |
| 27        | 60                  | 5                  | 20                   | 333             | 230.18               | 47.24     |
from 30.23 to 47.53. From Table 5 and Fig. 7, level 3 was found to be the best for each contact time and initial dye concentration factors, and level 1 was found to be the best for SnO$_2$/AC ratio and temperature factors. On the other hand, the order of importance of factors for the MB adsorption into SnO$_2$/AC nanocatalyst is initial dye concentration, contact time, SnO$_2$/AC ratio and temperature respectively, and the best uptake amount of MB dye is 237.96 mg g$^{-1}$ with ideal conditions.

### 3.4 Effect of contact time

From Fig. 7, it is clear that the contact time is an important parameter for the dye uptake. The S/N ratio increases by increasing the contact time from 15 min to 60 min and the highest MB uptake reached at contact time 60 min at third level. This may be due to of active sites and functional groups available on the surface of SnO$_2$/AC nanocatalyst at the beginning of the adsorption process.

### 3.5 Effect of initial MB dye concentration

To study the effect of MB initial concentration on the adsorption, different concentration of MB solutions (1, 2.5, 5 mM) were prepared. The results was put in Table 5 and represented in Fig. 7. The results shows that the S/N ratio increases by increasing the MB initial concentration and the highest MB uptake achieved at the third level of MB initial concentration (5 mmol). This may be due to a lot of pores and active sites on the surface of SnO$_2$/AC adsorbent are available.

### 3.6 Effect of temperature

The effect of temperature on the adsorption was investigated in three levels of temperature (293, 313, 333 K). The results which represented in Fig. 7 which shows that the S/N ratio decreases by increasing temperature.

In the other hands, the MB dye uptake decreases by increasing temperature and was achieved the lowest value at level 3 of temperature.

This may be due to the weak attraction between MB and adsorbent surface shown in Fig. 8, and the increasing of temperature leads to the MB molecules to escape from the surface [24, 25].

### 3.7 Effect of SnO$_2$/AC ratio

The obtained results show that the S/N ratio decreases by increasing of SnO$_2$/AC ratio. On the other words, the smallest S/N ratios value and the highest MB uptake occurred at ratio of 10 % SnO$_2$/AC. It means that the SnO$_2$/AC ratio is the least important variable influencing the dye uptake and the efficiency of MB dye adsorption decreases negligable with the increasing SnO$_2$/AC ratio. This may be due to the nanoparticles size SnO$_2$ is less than the size of micropores and loading more SnO$_2$ nanoparticles doesn't bloke the micropores, so the surface area of SnO$_2$/AC still large enough to affect the efficiency of MB adsorption very much.

### 4 Conclusion

An Activated Carbon modified tin oxide nanoparticle (SnO$_2$/AC) as a novel inexpensive nanocatalyst was synthesized and characterized. The new SnO$_2$/AC nanocatalyst balances many of the properties such as high surface area and effective adsorption power that researches have looking for, and could pave the way toward safe and environmentally friendlier alternatives for economical chemical industry. We find that the best conditions for the
adsorption of MB dye onto SnO₂/AC from solution were 10 % for SnO₂/AC ratio, 60 min for contact time, 5 mM for initial MB concentration and 298 K for temperature.

References

[1] Otsuka, K., Ogihara, K., Takenaka, S. "Decomposition of methane over Ni catalysts supported on carbon fibers formed from different hydrocarbons", Carbon, 41(2), pp. 223–233, 2003. https://doi.org/10.1016/S0008-6223(02)00308-1

[2] Ermakova, M. A., Ermakov, D. Y., Kuvshinov, G. G. "Effective catalysts for direct cracking of methan to produce hydrogen and filamentous carbon: Part I. Nickel catalysts", Applied Catalysis A: General, 20(1), pp. 61–70, 2000. https://doi.org/10.1016/S0926-860X(00)00433-6

[3] Liu, J., Zhao, Z., Xu, C., Duan, A., Zhu, L., Wang, X. "Diesel soot oxidation over supported vanadium oxide and K-promoted vanadium oxide catalysts", Applied Catalysis B: Environmental, 61(1–2), pp. 36–46, 2005. https://doi.org/10.1016/j.apcata.2005.04.006

[4] Chimentão, R. J., Herrera, J. E., Kwak, J. H., Medina, F., Wang, Y., Peden, C. H. F. "Oxidation of ethanol to acetaldehyde over Na-promoted vanadium oxide catalysts", Applied Catalysis A: General, 332(2), pp. 263–272, 2007. https://doi.org/10.1016/j.apcata.2007.08.024

[5] Nguyen, L. D., Loridant, S., Launay, H., Pigamo, A., Dubois, J. L., Millet, J. M. M. "Study of new catalysts based on vanadium oxide supported on mesoporous silica for the partial oxidation of methane to formaldehyde: Catalytic properties and reaction mechanism", Journal of Catalysis, 237(1), pp. 38–48, 2006. https://doi.org/10.1016/j.jcat.2005.10.016

[6] Tanaka, A., Yoon, S.-H., Mochida, I. "Formation of fine Fe–Ni particles for the non-supportive catalytic synthesis of uniform carbon nanofibers", Carbon, 42(7), pp. 1291–1298, 2004. https://doi.org/10.1016/j.carbon.2004.01.029

[7] Huwe, H., Fröba, M. "Synthesis and characterization of transition metal and metal oxide nanoparticles inside mesoporous carbon CMK-3", Carbon, 45(2), pp. 304–314, 2007. https://doi.org/10.1016/j.carbon.2006.09.021

[8] Huwe, H., Fröba, M. "Iron (III) oxide nanoparticles within the pore system of mesoporous carbon CMK-1: intra-pore synthesis and characterization", Microporous and Mesoporous Materials, 60(1–3), pp. 151–158, 2003. https://doi.org/10.1016/S1387-1811(03)00336-6

[9] Ding, Z., Hu, X., Zimmerman, A. R., Gao B. "Sorption and cosorption of lead (II) and methylene blue on chemically modified biomass", Bioresource Technology, 167, pp. 569–573, 2014. https://doi.org/10.1016/j.biortech.2014.06.043

[10] Tan, I. A. W., Ahmad, A. L., Hameed, B. H. "Adsorption of basic dye on high-surface-area activated carbon prepared from coconut husk: Equilibrium, kinetic and thermodynamic studies", Journal of Hazardous Materials, 154(1–3), pp. 337–346, 2008. https://doi.org/10.1016/j.jhazmat.2007.10.031

[11] Safa, Y., Bhatti, H. N. "Kinetic and thermodynamic modeling for the removal of Direct Red-31 and Direct Orange-26 dyes from aqueous solutions by rice husk", Desalination, 272, pp. 313–322, 2011. https://doi.org/10.1016/j.desal.2011.01.040

Acknowledgement

We gratefully acknowledge Hadhramout University for assist and support of the project presented in this article.
[22] Nunes, V. A., Guerreiro, M. C. "Estimation of Surface Area and Pore Volume of Activated Carbons by Methylene Blue and Iodine Numbers", Química Nova, 34(3), pp. 472–476, 2011. https://doi.org/10.1590/S0100-404220110003000020

[23] Bamsaoud, S. A., Rane, S. B., Karekar, R. N., Aiyer, R. C. "Nano particulate SnO$_2$ based resistive films as a hydrogen and acetone vapour sensor", Sensors and Actuators B: Chemical, 153(2), pp. 382–391, 2011. https://doi.org/10.1016/j.snb.2010.11.003

[24] Lee, E. J. H., Ribeiro, C., Giraldi, T. R., Longo, E., Leite, E. R. "Photoluminescence in quantum-confined SnO$_2$ nanocrystals: Evidence of free exciton decay", Applied Physics Letter, 84(10), pp. 1745–1747, 2004. https://doi.org/10.1063/j.snb.1.1655693

[25] Manna, S., Roy, D., Saha, P., Gopakumar, D., Thomas, S. "Rapid methylene blue adsorption using modified lignocellulosic materials", Process Safety and Environmental Protection, 107, pp. 346–356, 2017. https://doi.org/10.1016/j.psep.2017.03.008