



Int. J. New. Chem., 2020, Vol. 7, Issue 3, PP. 169-183.

International Journal of New Chemistry

Published online 2020 in <http://www.ijnc.ir/>
Open Access



Print ISSN: 2645-7237

Online ISSN: 2383-188x

Original Research Article

Removal of methylene blue by mesoporous CuO/SiO₂ as catalyst

Ali Reza Rahmani¹, Hossien Rahmani^{2*} and Afsaneh Zonouzi^{1*}

¹School of Chemistry, College of Science, University of Tehran, Tehran 14155-6455, Iran

²Department of Chemical Technologies, Iranian Research Organization for Science and Technology (IROST),
Tehran 3353-5111, Iran

Received: 2019-11-06

Accepted: 2020-01-15

Published: 2020-04-01

ABSTRACT

Among a wide range of pollutants, organic pollutants have given rise to major environmental concerns. Various methods have been considered to mitigate the damage, including catalytic reduction to less hazardous compounds. Catalysts that benefit from high surface area and suitable surface sites for various steps of the catalytic reaction have shown outstanding results in performing such duties. Mesoporous CuO/SiO₂ has been synthesized and characterized here and it showed excellent results for catalytic removal of methylene blue as a model organic pollutant. Several control samples were also studied to postulate a possible mechanism for activity enhancement.

Keywords: Reduction, Organic Pollutant, Nanoporous

Introduction

Serious environmental concerns have been raised regarding the improper disposal of wastewaters [1]. Amongst water pollutants, organic dyes are especially important due to the amount released and their hazard toward living organisms [2]. Such pollutants are mainly released by textile industry [3] among other sources. Many methods have been proposed to mineralize these compounds or at least break them into smaller less hazardous species, among these are the use of solid adsorbents [4, 5], catalysts [6, 7] and photocatalysts [8, 9]. Methylene blue (methylthioninium chloride) is an important drug (for methemoglobinemia treatment [10]) and dye with a wide range of applications including biological staining, redox indication, peroxide generation, etc. and has been used as a model dye in many pollutant removal studies [4, 8, 9].

In this research, CuO/SiO₂ was used for dye removal. One of the main approaches in catalyst engineering is placing them on suitable solid supports; various supports are known, SBA-15 is a well-known member of this family. This material was first synthesized by Zhao et al. [11, 12] at the University of California, Santa Barbara (the name stands for Santa Barbara Amorphous) and has been used as a support for catalysts [13-16] and photocatalysts [17-20] among various other applications [21-27]. Several approaches have been proposed to load different catalysts into SBA-15 [28]; among them post-synthetic methods are noteworthy. Although the final products obtained by post-synthetic grafting clearly lack the structural and chemical robustness necessary for consecutive reaction runs in environmental applications. As a compromise between robustness and activity, catalyst species have been incorporated into SBA-15 [29] for a variety of applications [30-33]. We have reported Cu/SBA-15 type catalyst for the synthesis of aryl diazenyl chromeno[2,3-d]pyrimidine derivatives [34], and Zn/SBA-15 as a regioselective catalyst for the synthesis of 5-aryl azo salicylaldehydes [35]. CuO/SiO₂ type materials with varying ratios have been widely studied for a wide range of applications. In 1996, Hadjiivanov et al. studied the adsorption of carbon monoxide CO on CuO/SiO₂ catalyst (with 1 wt% CuO) with an emphasis on σ and π components of the Cu⁺-CO bond by IR spectroscopy [36]; the same research team also proved the formation of new types of copper carbonyls in the same process later on [37]. Cordoba et al. studied the xerogel-glass transition of CuO/SiO₂ with various amounts using several characterization techniques [38]. In 1999, Díaz et al. synthesized CuO/SiO₂ with a sol-gel approach and used it as a nitrous oxide NO reduction catalyst [39]. Eliseev et al. used polycondensation of sodium silicate in an aqueous solution with Cu(II) polyvinyl alcohol

complex to obtain CuO/SiO₂ nanocomposites [40]. Sol-gel method was used by Zheng et al. to obtain CuO/SiO₂ with bimodal porous structure using poly (ethylene oxide) solvent and acetic acid as catalyst [41]. Sol-gel method was also used to obtain CuO/SiO₂ nanocomposite coatings on aluminum substrates [42]. CuO/SiO₂ catalyst which was obtained using precipitation-gel method proved to be active toward glycerol hydrogenolysis [43]. The effect of sol-gel parameters such as precursor concentration and thermal treatment regime on the final nanostructures of CuO/SiO₂ were studied by Tohidi et al. in 2010 [44]. Nanocomposites of the same type were also used as photocatalyst for methylene blue degradation under UV radiation [45] and as photoanode for dye-sensitized solar cells (DSSC) [46]. Its catalytic activity has been investigated for the synthesis of isobutyraldehyde from methanol and ethanol [47], decomposition of CO and NO [48], oxidizing ultra-low methane concentrations [49] as well as chemical looping air separation [50], and C–N cross-coupling of amines with aryl halides [51]. Furthermore, it was proved to have bactericidal activity toward *Pseudomonas aeruginosa* (a biofilm-forming microorganism) [52], the bactericidal activity of Cu²⁺ ions in CuO/SiO₂ nanocomposite also makes it possible to obtain multifunctional coatings for buildings stone [53].

Herein, we report the synthesis of mesoporous SBA-15 type CuO/SiO₂ as a catalyst for reductive removal of methylene blue as a model basic dye pollutant. Obtained catalyst showed excellent activity for dye removal in the presence of NaBH₄ as reducing agent and retained its activity after several runs of reaction without the need for any kind of activation process. Several control samples have also been studied to gain a deeper understanding of the activity enhancement mechanism for the main sample.

Experimental

Materials and methods

Tetraethylorthosilicate (TEOS), copper nitrate, HCl, methylene blue and malachite green were all from Merck (Germany) and P123 was obtained from Sigma-Aldrich (US). De-ionized water was used in all experiments. UV/Vis absorption spectra were recorded on a PG T80⁺ (UK) instrument. Scanning electron micrographs were obtained using SE and BSE detectors on a Zeiss DSM-960A (Germany) working at 30 kV. Field-emission scanning electron micrographs were obtained using a TSCAN MIRA 3 (Czech Republic) equipped with a Bruker XFlash 6130 (Germany) detector for EDX elemental mapping. Powder X-ray diffraction patterns were

recorded using a Philips PW1730 (Holland) instrument with CuK_α radiation.

Synthesis of CuO/SiO_2

Mesoporous CuO/SiO_2 catalyst was obtained using a previously reported method [34]. First, 1g of P123 (pluronic three-block co-polymer) was dissolved in 33 ml of HCl solution (2M) with magnetic stirring. After reaching a homogeneity, 2 g $\text{Cu(NO}_3)_2 \cdot 5\text{H}_2\text{O}$ was added and changed the color to blue upon dissolution. TEOS (2g) was then added slowly and vigorous stirring continued overnight at 40°C in a water bath. Afterwards, the reaction mixture was transferred to a Teflon-lined autoclave (100 mL) and heat treated at 100°C for 24 hours. After cooling down to room temperature in the oven (in the course of 24 hours), the obtained solid was centrifuged (at 5500 rpm with a Hettich, Germany instrument) and washed with de-ionized water several times until reaching neutral pH. The pre-ceramic product was transferred to an alumina boat and calcined at 450°C for 6 hours in a muffle furnace (Exciton, Iran). After annealing to room temperature (letting the sample cool down with the furnace itself over the course of one day), the obtained black powder was stored for characterization and catalytic activity evaluation.

Synthesis of control samples

Porous CuO sample was synthesized via an evaporation induced self-assembly (EIS) route. Firstly, 1 g of P123 was added to 40 ml of ethanol and dispersed by vigorous magnetic stirring at 75°C in a closed Pyrex vessel. Afterwards, 4g of $\text{Cu(NO}_3)_2 \cdot 5\text{H}_2\text{O}$ was added which made the solution turn color to brilliant blue. After complete dissolution, the reactor cap was removed and the solution was let to evaporate for one week. The blue xerogel was calcined at 450°C for 5 hours and annealed to room temperature. Obtained black CuO powder was stored for catalyst testing. CuO nanoparticles were obtained through a hydroxide approach [54]. Briefly, 1g of $\text{Cu(NO}_3)_2 \cdot 5\text{H}_2\text{O}$ was dissolved in 30 mL of water and titrated with NaOH solution. Obtained precursor was calcined at 450°C for 5 hours and stored for catalyst testing.

Catalytic and adsorption activity evaluation

Main and control samples were put to test for the reductive removal of methylene blue (MB) from aqueous media. In a typical run, 0.1 mg of catalyst along with 0.1 mg of NaBH_4 were

mixed with 2.5 mL of MB solution (5 ppm) in a quartz cell which was then placed inside a double-beam UV-Vis spectrophotometer and absorption spectra were recorded immediately and then in 90 second intervals (peak to peak time). For the adsorption experiments, all parameters were kept the same except the addition of NaBH_4 reducing agent which was omitted.

Results and discussion

Powder X-ray diffraction (XRD) pattern was obtained for the CuO/SiO_2 sample and it's presented in figure 1. Comparison of the peaks with PDF database proved the main phase of the sample to be CuO (01-080-1268) with monoclinic crystal structure [55] these peaks were indexed accordingly. None of the observed peaks are related to SiO_2 which can be attributed to the amorphous structure of this phase at the calcination temperature. This is in accordance with literature results [12]. Application of Scherrer's equation [56] to the obtained peaks gave average crystallite size of about 2.5 nm.

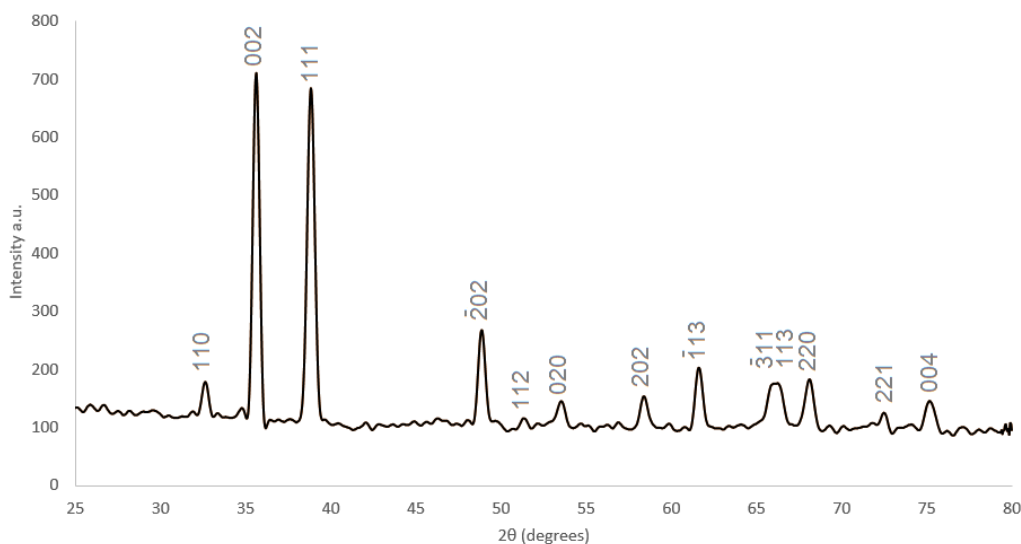


Figure 1. Powder XRD pattern for CuO/SiO_2 sample under study which is indexed due to 01-080-1268 reference pattern related to monoclinic CuO .

Scanning electron microscopy (SEM) was used with both SE and BSE detectors the results of which are presented in parts a and b of figure 2, respectively. Secondary electron micrograph (SE) elucidates the morphological structure of the sample under study in micrometer length scale while backscattered electron micrograph (BSE) presents an atomic number contrast. Comparing

the two shows no segregation of heavier atoms at least in this scale and the sample seems to be uniform.

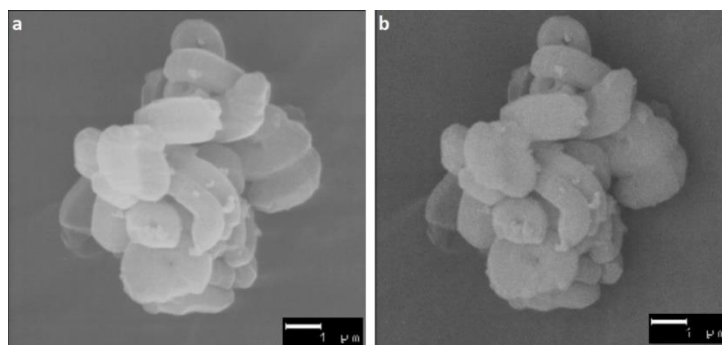


Figure 2. Scanning electron micrographs of CuO/SiO₂ sample with SE (a) and BSE (b) signals

In order to gain a deeper understating of the morphology of the main sample under study, field emission scanning electron microscopy (FESEM) was used and the micrographs are presented in Figure 3. Comparing the micrographs of figures 2 and 3 shows that in higher resolutions, morphological differences are observable. Based on XRD results, the well-defined particles seem to be CuO while the fuzzy motifs may be SiO₂, although this differentiation is not conclusive.

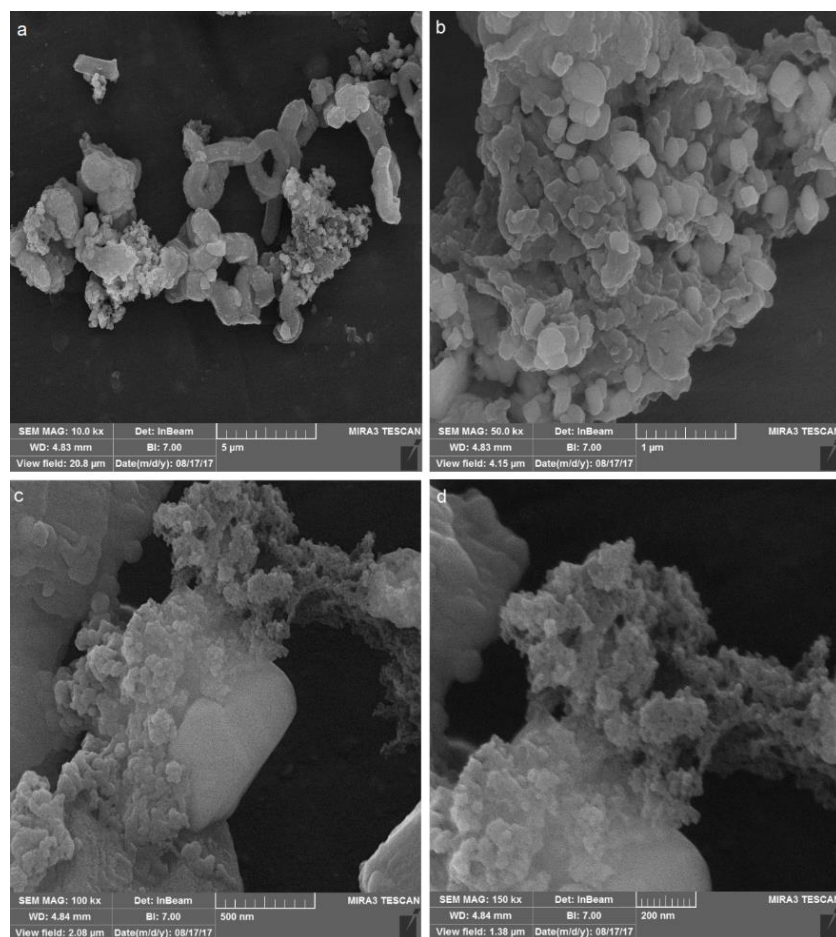


Figure 3. Field-emission scanning electron micrographs of CuO/SiO₂ sample at different magnifications.

EDX elemental maps were also recorded for CuO/SiO₂ under study and the results for Si, O and Cu distribution at 2000X are presented in figure 4. As with the BSE image of figure 2, no micron scale elemental segregation is observed, but this does not prove the sample to be comprised of a solid solution. XRD results conclusively prove the existence of well-defined CuO phase.

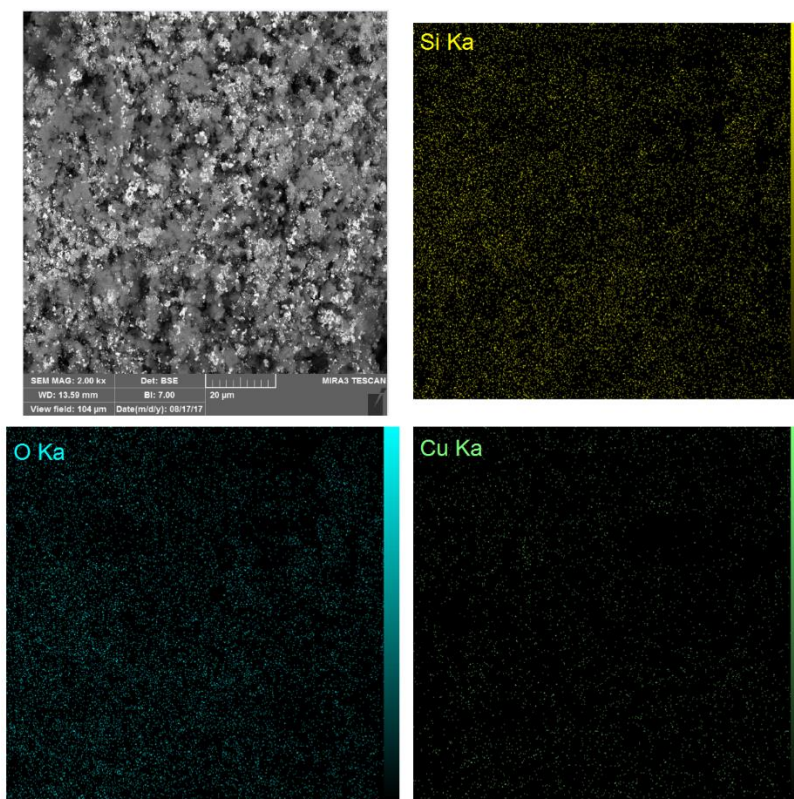


Figure 4. EDX elemental maps for CuO/SiO₂ sample under study.

When interpreting adsorption isotherms, t-plot is a frequently used technique [57]. In this approach, absorption amount is expressed in terms of absorption layer thickness (t) and the resulting plots are compared to reference curves. Unlike adsorption-desorption curves, there are no IUPAC definitions for such curves, but they are normally categorized into three types for convenience. Type I is related to non-porous materials, while type II is obtained from microspores with homogeneous size. Type III on the other hand is characteristic of mesoporous solids and the observed deviation from linearity (Figure 5) shows capillary condensation.

In a standard type III curve, the low “ t ” slope gives the pore area, while the middle part is related to the volume of mesopores and the high “ t ” slope is the external area. In the presented sample (Figure 5), the external surface area is calculated to be $26.249 \text{ m}^2\text{g}^{-1}$, while the pore surface area is $176.48 \text{ m}^2\text{g}^{-1}$. Combined surface area is somehow lower than the BET surface area ($231.15 \text{ m}^2\text{g}^{-1}$) which is due to overestimation by the later method.

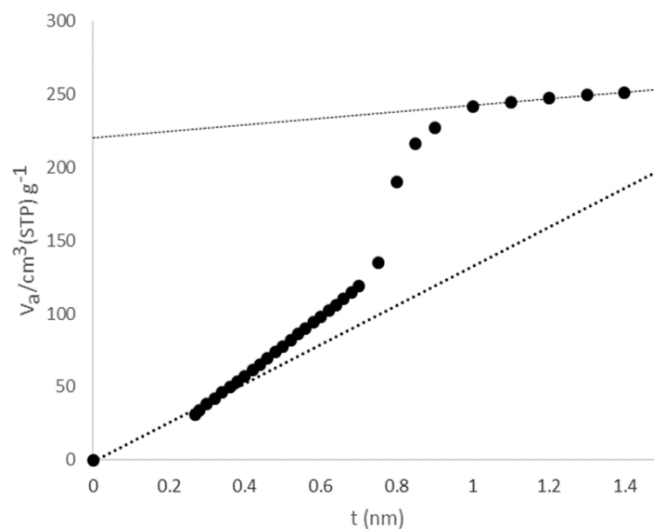
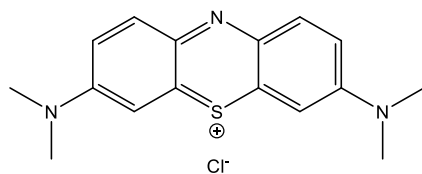


Figure 5. t-plot for the mesoporous CuO/SiO₂ under study which clearly shows type III standard behaviour, characteristic of mesoporous samples.

Catalytic ability of CuO/SiO₂ sample was evaluated for the reductive removal of methylene blue (MB) dye from aqueous media. In order to gain a deeper understanding regarding the roles of CuO and SiO₂ phase in the catalyst, control samples were designed for comparison. The synthetic methods are different for these samples and are included in the experimental section.

The rationale behind choosing CuO/SiO₂ for reductive methylene blue removal can be categorized into two mechanism. Firstly, copper-based catalysts have been well known to catalyze such reactions as we have shown in previous reports [6, 7] and they act by enhancing the hydrogen evolution reaction from NaBH₄. On the other hand, SiO₂ is known to provide acidic surface sites which are perfect for adsorbing basic molecules of methylene blue dye. Acid-base properties of copper catalyst support has been studied in the past and proved to have a co-catalyst effect toward reactions such as CO₂ hydrogenation [58] and NO reduction by C₂H₄ [59]. In order to prove the aforementioned theories, we have designed several tests based on catalytic as well as adsorptive dye removal in a reasonable time scale, the results are presented below.

Time-dependent adsorption experiments were performed similar to catalytic dye removal without the addition of NaBH₄. Methylene blue (MB) was used as a model basic dye (scheme 1). As can be observed from figure 6, the same amount of porous CuO/SiO₂ could absorb about 15 molar percent of MB over the course of 30 minutes.



Scheme 1. Chemical structures of methylene blue

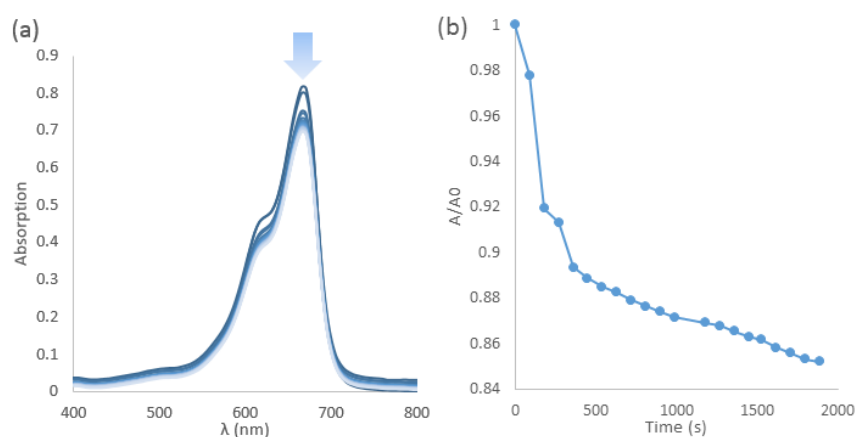


Figure 6. Time dependent UV-Vis spectra for the adsorption capacity of CuO/SiO₂ toward MB (a) along with the related variation of absorption intensity at λ_{\max} with time (b).

The chemical environment of the copper species can also play a crucial role in determining the activity of the final catalyst for dye removal (figure 7). SBA-15 decorated with metallic copper nanoparticles shows a faster reaction rate at start compared to pristine SBA-15, but ultimately the removal efficiency was similar (part a). Porous CuO (part b) and unsupported CuO nanoparticles (part c) on the other hand showed a better activity, but were not drastically different in the long run.

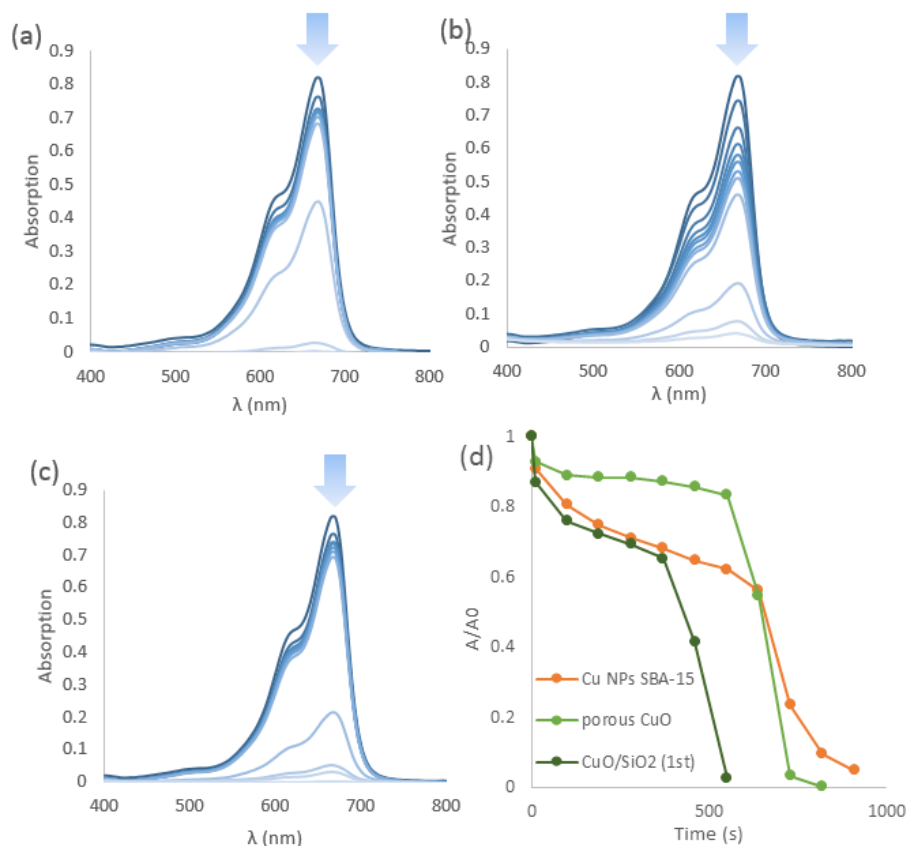


Figure 7. Time dependent UV-Vis spectra for reductive removal of MB with catalysts: Cu NPs@SBA-15 (a), porous CuO (b), Cu NPs (c) along with the related variation of absorption intensity at λ_{max} with time (d).

A robust catalyst especially for environmental application should withstand several runs of reaction preferably without the need for recovery protocols. CuO/SiO₂ catalyst under study is no exception and the re-use test was performed for at least 5 times for this catalyst and showed no meaningful decrease in removal activity (the results of the first 2 runs are presented in figure 8).

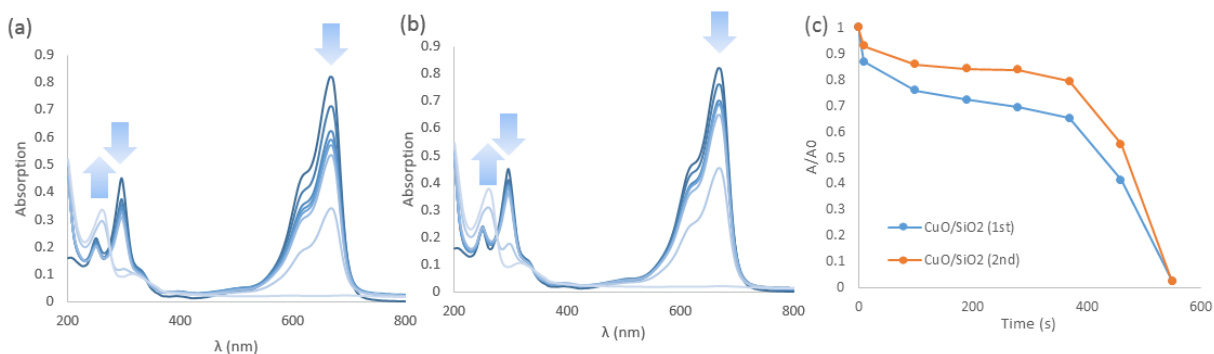


Figure 8. Time dependent UV-Vis spectra for reductive removal of MB with CuO/SiO₂ catalyst at first run (a) and second run (b) along with the related variation of absorption intensity at λ_{\max} with time (c).

Conclusion

Mesoporous CuO/SiO₂ was synthesized using hydrothermal method and characterized with various techniques including XRD, SEM, FESEM, EDX, and N₂-physisorption. The acidic nature of surface sites and the catalytic nature of copper species gave rise to excellent removal activity toward methylene blue reduction as a model basic dye. Several control samples were also synthesized and put to test in order to represent the unique activity of the presented catalyst for this model environmental reaction.

Acknowledgments

The authors wish to thank University of Tehran and Iranian research organization for science and technology (IROST) for financial support.

References

- [1] G. Tchobanoglous, F.L. Burton, H. Stensel, *Management*, 7, 1 (1991).
- [2] L. Pereira, M. Alves, *Dyes—environmental impact and remediation*, in *Environmental protection strategies for sustainable development*, Springer, (2012).
- [3] F.D. Chequer, G.A.R. de Oliveira, E.A. Ferraz, J.C. Cardoso, M.B. Zanoni, D.P. de Oliveira, *Eco-friendly textile dyeing and finishing*, IntechOpen (2013).
- [4] H.B.M. Emrooz, M. Maleki, A. Rahmani, *J. Taiwan Inst. of Chem. E.*, 91, 281 (2018).
- [5] H.B.M. Emrooz, M. Maleki, M. Shokouhimehr, *J. Taiwan Inst. of Chem. E.*, 102 (2019).
- [6] A. Rahmani, H. Rahmani, A. Zonouzi, *Mater. Res. Express*, 4, 125024 (2017).
- [7] A. Rahmani, H. Rahmani, A. Zonouzi, *Chem. Pap.*, 72, 449 (2018).
- [8] H.B.M. Emrooz, A. Rahmani, *Mat. Sci. Semicon. Proc.*, 72, 15 (2017).
- [9] H.B.M. Emrooz, A.R. Rahmani, F.J. Gotor, *Aust. J. Chem.*, 70, 1099 (2017).
- [10] Joint Formulary Committee, *British national formulary (BNF) Vol. 66*. Pharmaceutical Press (2013).
- [11] D. Zhao, J. Sun, Q. Li, G.D. Stucky, *Chem. Mater.*, 12, 275 (2000).

- [12] D. Zhao, J. Feng, Q. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka, G.D. Stucky, *Science*, 279, 548 (1998).
- [13] R. Rioux, H. Song, J. Hoefelmeyer, P. Yang, G. Somorjai, *J. Phys. Chem. B*, 109, 2192 (2005).
- [14] Y.-M. Liu, Y. Cao, N. Yi, W.-L. Feng, W.-L. Dai, S.-R. Yan, H.-Y. He, K.-N. Fan, *J. Catal.*, 224, 417 (2004).
- [15] T.I. Korányi, Z. Vít, D.G. Poduval, R. Ryoo, H.S. Kim, E.J. Hensen, *J. Catal.*, 253, 119 (2008).
- [16] Y. Wang, M. Noguchi, Y. Takahashi, Y. Ohtsuka, *Catal. Today*, 68, 3 (2001).
- [17] S. Perathoner, P. Lanzafame, R. Passalacqua, G. Centi, R. Schlögl, D.S. Su, *Micropor. Mesopor. Mat.*, 90, 347 (2006).
- [18] M.-J. López-Muñoz, R. van Grieken, J. Aguado, J. Marugán, *Catal. Today*, 101, 307 (2005).
- [19] H. Ding, H. Sun, Y. Shan, *J. Photochem. Photobiol. A*, 169, 101 (2005).
- [20] G. Mihai, V. Meynen, M. Mertens, N. Bilba, P. Cool, E. Vansant, *J. Mater. Sci.*, 45, 5786 (2010).
- [21] H.H. Yiu, P.A. Wright, N.P. Botting, *J. Molec. Catal. B*, 15, 81 (2001).
- [22] A. Vinu, V. Murugesan, M. Hartmann, *J. Phys. Chem. B*, 108, 7323 (2004).
- [23] L. Fagundes, T. Sousa, A. Sousa, V. Silva, E. Sousa, *J. Non-Cryst. Solids*, 352, 3496 (2006).
- [24] H.H. Yiu, C.H. Botting, N.P. Botting, P.A. Wright, *Phys. Chem. Chem. Phys.*, 3, 2983 (2001).
- [25] N. Hiyoshi, K. Yogo, T. Yashima, *Micropor. Mesopor. Mater.*, 84, 357 (2005).
- [26] A.C. Chang, S.S. Chuang, M. Gray, Y. Soong, *Energ. Fuel.*, 17, 468 (2003).
- [27] A. Katiyar, S. Yadav, P.G. Smirniotis, N.G. Pinto, *J. Chromatogr. A*, 1122, 13 (2006).
- [28] R. Huirache-Acuña, R. Nava, C. Peza-Ledesma, J. Lara-Romero, G. Alonso-Núñez, B. Pawelec, E. Rivera-Muñoz, *Materials*, 6, 4139 (2013).
- [29] W.-H. Zhang, J. Lu, B. Han, M. Li, J. Xiu, P. Ying, C. Li, *Chem. Mater.*, 14, 3413 (2002).
- [30] L. Wang, A. Kong, B. Chen, H. Ding, Y. Shan, M. He, *J. Molec. Catal. A*, 230, 143 (2005).

- [31] X. Wang, K.S. Lin, J.C. Chan, S. Cheng, *J. Phys. Chem. B*, 109, 1763 (2005).
- [32] D. Margolese, J. Melero, S. Christiansen, B. Chmelka, G. Stucky, *Chem. Mater.*, 12, 2448 (2000).
- [33] L. Fuxiang, Y. Feng, L. Yongli, L. Ruifeng, X. Kechang, *Micropor. Mesopor. Mater.*, 101, 250 (2007).
- [34] A. Zonouzi, H.A. Shahrezaee, A. Rahmani, F. Zonouzi, K. Abdi, F.T. Fadaei, K. Schenk, *Org. Prep. Proc. Int.*, 50, 343 (2018).
- [35] F. Zonouzi, A. Rahmani, H. Dezhampanah, B. Ghalami-Chooobar, A. Zonouzi, *Chem. Pap.*, 73, 2409 (2019).
- [36] K.I. Hadjiivanov, M.M. Kantcheva, D.G. Klissurski, *J. Chem. Soc. Faraday Trans.*, 92, 4595 (1996).
- [37] K. Hadjiivanov, T. Venkov, H. Knözinger, *Catal. Lett.*, 75, 55 (2001).
- [38] G. Cordoba, R. Arroyo, J.L.G. Fierro, M. Viniegra, *J. Solid State Chem.*, 123, 93 (1996).
- [39] G. Díaz, R. Pérez-Hernández, A. Gómez-Cortés, M. Benaissa, R. Mariscal, J.L.G. Fierro, *J. Catal.*, 187, 1 (1999).
- [40] A.A. Eliseev, A.V. Lukashin, A.A. Vertegel, L.I. Heifets, A.I. Zhironov, Y.D. Tretyakov, *Mat. Res. Innov.*, 3, 308 (2000).
- [41] M. Zheng, T. Zhao, W. Xu, F. Li, Y. Yang, *J. Sol-Gel Sci. Technol.*, 39, 151 (2006).
- [42] Q. Yu, X. Ma, M. Wang, C. Yu, T. Bai, *App. Sur. Sci.*, 254, 5089 (2008).
- [43] Z. Huang, F. Cui, H. Kang, J. Chen, C. Xia, *Appl. Catal. A*, 366, 288 (2009).
- [44] S.H. Tohidi, G. Grigoryan, V. Sarkeziyan, F. Ziaie, *Iran. J. Chem. and Chem. Eng.*, 2010, 29, 27 (2010).
- [45] A.P.L. Batista, H.W.P. Carvalho, G.H.P. Luz, P.F.Q. Martins, M. Gonçalves, L.C.A. Oliveira, *Env. Chem. Lett.*, 8, 63 (2010).
- [46] T. Tenkyong, N. Bachan, J. Raja, P.N. Kumar, J.M. Shyla, *Mater. Sci. Poland*, 33, 826 (2015).
- [47] L. Cuigai, W. Jing, W. Kangjun, L. Haihua, *Petrochem. Technol.*, 5 (2011).
- [48] V. Homaunmir, S.H. Tohidi, G. Grigoryan, *Iran. J. Chem. Chem. Eng.* 32, 37 (2013).
- [49] Y. Zhang, E. Doroodchi, B. Moghtaderi, *Appl. Energy*, 113, 1916 (2014).
- [50] H. Song, K. Shah, E. Doroodchi, T. Wall, B. Moghtaderi, *Energ. Fuel.*, 28, 173 (2014).

- [51] A.R. Hajipour, F. Dordahan, F. Rafiee, M. Mahdavi, *Appl. Organometall. Chem.*, 28, 809 (2014).
- [52] M. Nowacka, A. Modrzejewska-Sikorska, Ł. Chrzanowski, D. Ambrożewicz, T. Rozmanowski, K. Myszka, K. Czaczyk, K. Bula, T. Jesionowski, *Bioelectrochem.*, 87, 50 (2012).
- [53] R. Zarzuela, M. Carbú, M.L.A. Gil, J.M. Cantoral, M.J. Mosquera, *Mater. Design*, 114, 364 (2017).
- [54] D.P. Singh, A.K. Ojha, O.N. Srivastava, *J. Phys. Chem. C*, 113, 3409 (2009).
- [55] N. Brese, M. O'keeffe, B. Ramakrishna, R. Von Dreele, *J. Solid State Chem.*, 89, 184 (1990).
- [56] P. Scherrer, Bestimmung der inneren Struktur und der Größe von Kolloidteilchen mittels Röntgenstrahlen, in *Kolloidchemie Ein Lehrbuch*, Springer, 387-409, (1912).
- [57] B.C. Lippens, J. De Boer, *J. Catal.*, 4, 319 (1965).
- [58] N. Nomura, T. Tagawa, S. Goto, *Reac. Kinet. Catal. Lett.*, 63, 21 (1998).
- [59] A. Gervasini, M. Manzoli, G. Martra, A. Ponti, N. Ravasio, L. Sordelli, F. Zaccheria, *J. Phys. Chem. B*, 110, 7851 (2006).

How to Cite This Article

Ali Reza Rahmani, Hossien Rahmani, Afsaneh Zonouzi¹, "Removal of methylene blue by mesoporous CuO/SiO₂ as catalyst" *International Journal of New Chemistry.*, 2020; 7(3), 169-183. DOI: 10.22034/ijnc.2019.116043.1060