Degradation of Crystal Violet Dye from Waters by Layered MnO$_2$ and Nanocomposite-MnO$_2$@MnFe$_2$O$_4$ Catalysts

Sulardaki Kristal Moru Boyasının Tabakalı MnO$_2$ ve MnO$_2$@MnFe$_2$O$_4$ Nanokompozit Katalizörleri ile Parçalanması

Research Article

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ABSTRACT

In this study, the removal and degradation of a basic triphenylmethane dye "crystal violet" (CV) was investigated by using layered MnO$_2$ and MnO$_2$@MnFe$_2$O$_4$ nanocomposite catalysts in aqueous solutions in the presence of H$_2$O$_2$. The reaction was faster with the layered MnO$_2$. The catalytic degradation of CV was traced by analyzing the degradation products using Electrospray Ionization-Quadrupole-Time-of-Flight-Mass Spectrometry (ESI-Q-ToF-MS). 4-isocyanobenzaldehyde (A) and Michler's ketone (B) were identified as main intermediates both of which can potentially be bioremediated to mineralization products. MnO$_2$/H$_2$O$_2$ thus appeared to be an encouraging catalyst system in converting CV to biodegradable fragments.

Key Words
Crystal violet, dye degradation, catalytic oxidation, manganese oxide catalysts.

ÖZ

Bu çalışmada, bazik bir trifenilmetan boyası olan "kristal moru"nun (CV) sulu çözeltilerde H$_2$O$_2$ varlığında uzaklaştırılması ve bozunması, tabakalı MnO$_2$ ve ayrıca MnO$_2$@MnFe$_2$O$_4$ nanokompozit katalizörler kullanılarak araştırıldı. CV'nin bozunmasının tabakalı MnO$_2$ yapısı ile daha hızlı gerçekleştiği görüldü. Katalitik bozunma ürünleri Elektrospray İyonlaşmalı-Dört Kutuplu-Uçuş Zamanlı Kütle Spektrometresi (ESI-Q-ToF-MS) kullanılarak izlendi ve analiz edildi. Ana parçalanma ürünleri olarak, biyo-iyileştirme ile mineralizasyon ürünlerine dönüşebilme potansiyeli olan 4-izosiyanobenzaldehit (A) ve Michler ketonu (B) tanımlandı. Böylece, MnO$_2$/H$_2$O$_2$ sisteminin CV'yi biyobozunabilir yapılara dönüştürebilen özendirici bir katalizör olduğu anlaşıldı.

Anahtar Kelimeler
Kristal moru, boya bozunumu, katalitik oksidasyon, manganoksit katalizörleri.

INTRODUCTION

Dyes are complex organic compounds which are commonly used in textile, paper, printing, carpet, plastic, food and cosmetic industries. The treatment of wastewater in these industries is a serious environmental problem as ca. 40.000-50.000 tonnes of dye-pollutants are annually discharged to waters. Common treatment methods for dye-polluted water include adsorption, biodegradation, coagulation, oxidation, ozonolysis and membrane processes, each one having its own advantages and limitations [1]. The traditional physical methods which transform organic subtances to other forms are quite expensive. Recents studies are therefore directed to the development of more efficient techniques towards the complete mineralization of the dye by oxidation of carbon to CO_2, nitrogen to NO_3^- and hydrogen to H_2O with environment-friendly catalysts [2,3].

Many heterogeneous systems composed of hydrogen peroxide and a metal oxide have been reported to perform better than homogeneous systems for catalytic degradation of dyes [4,5]. Among the metal oxide based heterogeneous systems, manganese oxides have been widely applied as catalysts in waste water treatment. Porous manganese oxides with variable manganese oxidation states and in various polymorphic forms are active oxidants for organic molecules and functional groups [6]. Segal and Suib reported the degradation of "pinocyanol chloride dye" with octahedral molecular sieves prepared by doping porous manganese oxides with Fe^{3+}, Co^{2+} and Cr^{3+} [7]. The same researchers later studied the degradation of "methylene blue" with these doped manganese oxides in the presence of peroxide and introduced the method as a versatile and green approach [8]. MnO_2 photo-catalyzed the degradation of Bengal Pink acting as a semi-conductor forming hydroxyl radicals (OH·) through positive holes [9]. Kannan et al. demonstrated decolorization of "methylene blue" and "amido black" dyes with layered- and octahedral manganese oxides in the presence of hydrogen peroxide[10]. Ultrasonic radiation was found to enhance the activity of MnO_2 catalyst in the degradation of "acid red B" [11]. Various dyes were shown to adsorb on diatomite-supported manganese oxides via surface adsorption and intercalation mechanisms [12].

Magnetic nanocatalysts have recently gained attention in the field of heterogeneous catalysis with respect to classical homogeneous catalysts due to their unique surface properties, high surface areas and easy separation from the reaction medium by means of an external magnetic field. Core-shell structured $Fe_3O_4@K_xMnO_2$ nanocomposite has been suggested as a powerful adsorbant for organic dye pollutants [13] however dye degradation reports with such systems are very limited to the authors' knowledge.

CV is a triphenylmethane dye (Scheme 1) and is most widely used for the dyeing of cotton, wool, silk, nylon, paper, leather etc. Like many other basic dyes, CV is toxic and poses a threat to the environment [14]. Metal oxide catalysts employed so far for the removal/degradation of this dye include ZnO [15], Fe_3O_4 [16], polytungstonickelate [17] and nano-Mn_3O_4 [18]. All of these studies suggest a Fenton-type oxidation mechanism proceeding through hydroxyl radicals generated by photocatalysis or from peroxide [19,20]. This work is aimed to investigate the implications of birnessite type layered-nano-MnO_2 and core-shell nanocomposite $MnO_2@MnFe_2O_4$ catalysts in the degradation of CV in the presence of H_2O_2 (Scheme 1).

MATERIALS and METHODS

Materials

Crystal violet was obtained from Sigma–Aldrich and used without any further purification (λ_{max}: 589 nm at pH= 6). The reactions were conducted in deionized water. Hydrogen peroxide (30%) was obtained from Merck.

Synthesis of Layered MnO_2, $MnFe_2O_4$ Core Material and $MnO_2@MnFe_2O_4$ Core-shell Nanocomposite

Layered MnO_2, $MnFe_2O_4$ core, and the $MnO_2@MnFe_2O_4$ nanocomposite were prepared according to our previous synthetic protocol [21,22] and characterized by X-ray diffraction (XRD) and electron microscopy techniques.

Powder XRD patterns were recorded using a Rigaku D/MAX-2200 diffractometer equipped with graphite-filtered Cu Kα radiation (λ=1.54056 Å) from 3 to 70° (2θ) at a scanning rate of 2° min^{-1}. Fi-
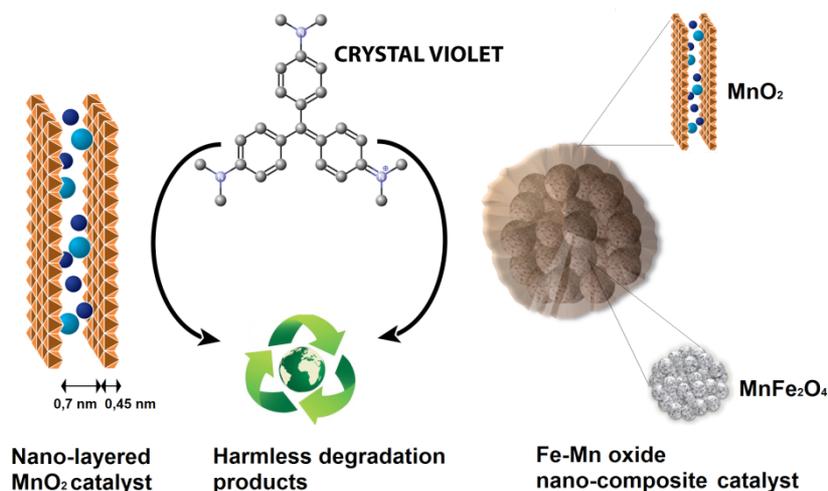
Scheme 1. Description of degradation of CV by nano-MnO$_2$ catalysts.

eld-emission scanning electron microscopy (SEM) images were recorded using a FEI Quanta 200 FEG instrument and high-resolution analytical transmission electron microscopy (TEM) images were recorded with a FEI Tecnia G2 F30 instrument operating at 300 or 100 kV.

MnFe$_2$O$_4$ Core Material: 0.70 g of KMnO$_4$, 3.13 g of Fe(NO$_3$)$_3$·9H$_2$O, 0.90 g of polyvinylpyrrolidone (PVP), and 5.97 g of NaOAc were dissolved in 60 mL of ethylene glycol and homogenized by vigorous stirring for 30 min. The resulting solution was transferred to a teflon-lined stainless steel autoclave and maintained at 200°C for 5 h. The black precipitate was separated by a magnet, washed with water, and then dried in an oven at ca. 70°C.

MnO$_2$@MnFe$_2$O$_4$: 1g of MnFe$_2$O$_4$ was sonicated for 30 min in 100 mL of deionized water. Then, 1g of KMnO$_4$ and 0.5 mL of concentrated propionic acid were slowly added with vigorous stirring. The solution was stirred mechanically and refluxed at 90°C for 1h. The product, MnO$_2$@MnFe$_2$O$_4$, was separated using a magnet, thoroughly washed with deionized water and dried at 65°C for 24 h.

Layered MnO$_2$: The plain catalyst was prepared by the method described above but without supporting over MnFe$_2$O$_4$ particles.

Dye Degradation Studies
Catalytic dye degradation studies were carried out at room temperature in an open batch reactor with continuous stirring and dye oxidation was followed by observing decolorization of the reaction solution.

The optimal pH value at which the degradation reaction proceeds while the catalyst maintains its stability was found to be 5-6 after recording the UV/Vis spectra of solutions between pH 6-11. The pH was adjusted to 6 by addition of HCl/NaOH to a mixture of dye, peroxide and catalyst and a series of degradation reactions were performed by changing the dye/catalyst/H$_2$O$_2$ ratios to investigate the dye degradation efficiencies of the catalysts. During the entire process, pH was not readjusted and no buffer solution was used. The use of buffer seemed not to have any significant effect on the reaction between peroxide and manganese species. Blank experiments were run under similar conditions but without using peroxide. After a given time interval, 5.0 μL of the mixture solution was pipetted out, micropore filtered and analyzed.

Mass Spectrometry
Analyses of samples were carried out using Agilent 6530 Accurate-Mass Q-ToF-MS instrument equipped with Agilent Jet Stream (AJS) ESI source (Agilent Technologies, USA). Solutions of samples were diluted with a 1:1 (v/v) mixture of water and methanol. The sample solutions were directly infused into the ESI source at a flow rate of 10 μL/min. Mass spectra were acquired in the high-resolution mode (4 GHz, High Res Mode) at

100-3200 m/z range. Analyses were performed in positive ion mode using the following settings: both drying and sheath gas (nitrogen) temperatures were set as 350°C at 10 L/min flow rate, nebulizer pressure at 40 psi, capillary voltage at 4000 V, and fragmentor voltage at 175 V. Both centroid and profile data were acquired with Agilent Mass Hunter workstation software.

RESULTS and DISCUSSION

Figure 1 shows the XRD patterns of the prepared catalysts. The diffraction peaks for $MnFe_2O_4$ at 18.3°, 30.2°, 35.5°, 36.9°, 43.1°, 53.5°, 57.0°, and 62.6° correspond to the respective (111), (220), (311), (222), (400), (422), (511), and (440) planes of the spinel type nanostructured manganese ferrite (JCPDS Card no. 17-465). The diffraction peaks for MnO_2 at about 12°, 25° and 37° match the typical XRD pattern of birnessite-type manganese oxide structure (JCPDS 80-1098). The pattern for the nanocomposite catalyst contains reflections corresponding to both MnO_2 (+) and $MnFe_2O_4$ (*) components.

SEM and TEM images further verified the structures of the catalysts. The SEM image (A) in Figure 2 shows the cotton ball-like particles of MnO_2 with diameters smaller than 1 μm and the TEM image (B) shows that the cotton-ball-like particles appear to link together to form larger particles. In Figure 2. (C) and (D) show the SEM and TEM images of MnO_2@$MnFe_2O_4$, respectively. SEM image indicates a nearly spherical morphology of nanocomposite particles and the TEM image clearly shows the core–shell architecture where MnO_2 nanoflakes were homogeneously coated on the $MnFe_2O_4$ core.

Degradation of CV with the Layered MnO_2 Catalyst

Catalytic performance of the layered MnO_2 was tested by degrading of 200 ppm CV solution with 5 mg of the catalyst. H_2O_2 was added dropwise (0.2 μL/min) and complete decolorization was observed in 20 min (Figure 3).

A blank run with the above conditions showed no appreciable decolorization of the solution. Use of the catalyst or H_2O_2 alone was not efficient. A

Figure 1. Powder XRD patterns of the core material: $MnFe_2O_4$; the shell: MnO_2 and the corresponding nanocomposite: MnO_2@$MnFe_2O_4$.
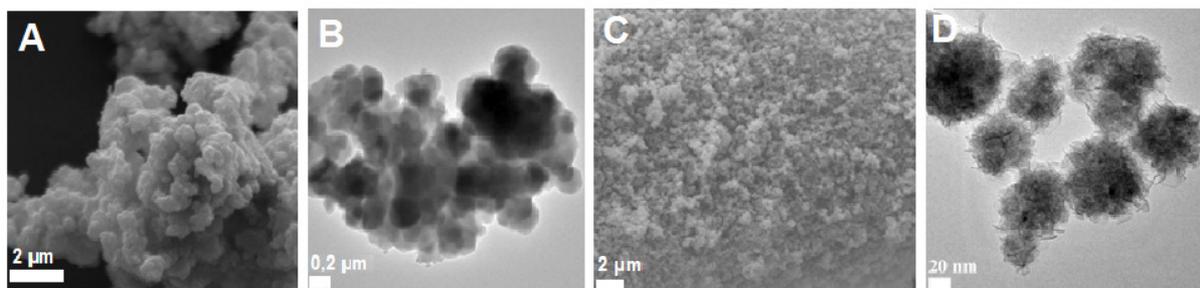
Figure 2. SEM and TEM images of layered MnO_2 (A,B) and MnO_2@$MnFe_2O_4$ (C,D) nanocomposite catalysts.

Figure 3. Progressive decolorization of CV solution in 20 min with the MnO_2/H_2O_2 catalyst.

radicalic oxidative pathway could be where degradation is initiated by hydroxyl attack on the CV molecule followed by N-demethylation and cleavage to smaller fragments, as reported for the Fe/H_2O_2 system (Fan et al. 2009). However, amorphous and crystalline manganese oxides were reported to catalyze the decomposition of H_2O_2 to reductants ($O_2^{\cdot-}$, HO_2^-, H·) where hydroxyl radicals are not generated. Decomposition proceeds not only directly on the surface of manganese oxide, but also through a propagation reaction involving intermediates such as hydroperoxide/superoxide anion in solution [23,24]. So, a reductive pathway through a nonhydroxyl radical could therefore be possible here for CV degradation.

Dye degradation profile was investigated by monitoring the ESI-MS spectra of samples withdrawn from the reaction medium at specified time intervals (Figure 4). Non-degraded CV gives a molecular ion peak at m/z 372.25 and a low intensity signal at m/z 358.25 corresponding to an N-demethylated product. After 1 h of reaction time, the signal at m/z 372.25 disappeared suggesting that the dye was completely decomposed to smaller fragments. The main degradation products were assigned as 4-isocyanobenzaldehyde (observed at m/z 130.16) (A) and 4, 4'-bis(dimethylaminobenzophenone) (m/z 269.17) (B). Compound B is the well-known Michler's ketone which has been reported as one of the main intermediates among the biodegradation and chemical degradation products of CV [5,20]. B is formed by the cleavage of the chromophore structure after radical attack on the conjugated skeleton. As the reaction proceeded, intensity of the m/z 269.17 peak decreased while N-demethylation peaks regularly appeared at m/z 15 differences (including the one at m/z 240.16). Some new peaks appeared above m/z 500 due to the polymerization of small fragments in time.

In addition to the benzophenone formation and N-demethylation degradation route described above, an alternative pathway would be suggested when the ESI-MS spectra were analyzed (Scheme 2). The signal at m/z 130.16 was persistent in all spectra recorded periodically over 24 h and was noticed for the first time in the degradation of CV ever reported, to our knowledge. Hydrogen atom attached to the carbonyl group of an aldehyde molecule tends to be expelled to form a stable acylium ion in the gas phase. Therefore, aldehydes have an intense $[M–H]^+$ peak in the mass spectra. We assigned this signal as the $[M-H]^+$ peak of 4-isocyanobenzaldehyde (A). So, a plausible mechanism for the formation of (A) could be suggested as follows: hydroperoxide/ superoxide anion radicals attack on the central carbon atom of the chromophore structure cleaving CV into two fragments. An aldehyde group is formed on the central atom while aromatization of the cyclohexadiene ring, N-demethylation of the quaternary nitrogen and conversion to isonitrile structure yields (A). The second fragment, N,N,N',N'-tetramethylbiphenyl-4,4'-diamine, is formed by coupling of two N,N-dimethylaniline radicals and having signals at m/z value of 240.16. Further degradation leads to formation of other products which will not be discussed here because CV rapidly degrades to two main fragments, (A) and Michler's ketone, both of which are biodegradable.

Michler's ketone degrades naturally when released into the soil, water and air by sun irradiation and microbes in aquatic environments [25]. On the other hand, C≡N moiety containing compound (A) is a member of the toxic nitrile family but can be eliminated by microbial degradation. Researchers from Japan reported two new enzymes for C≡N bond cleavage and clarified the degradation pathway. Isonitrile hydratase catalyzes hydration of isonitrile to N-substituted formamide which then converts to amine and formate by formamidedeformylase [26,27].

Although the degrading rate of the catalyst was quite high, degradation efficiency was limited with the first use. It is known that MnO_x catalysts are not recyclable in Fenton-like systems where the reaction with H_2O_2 causes deactivation of the catalyst
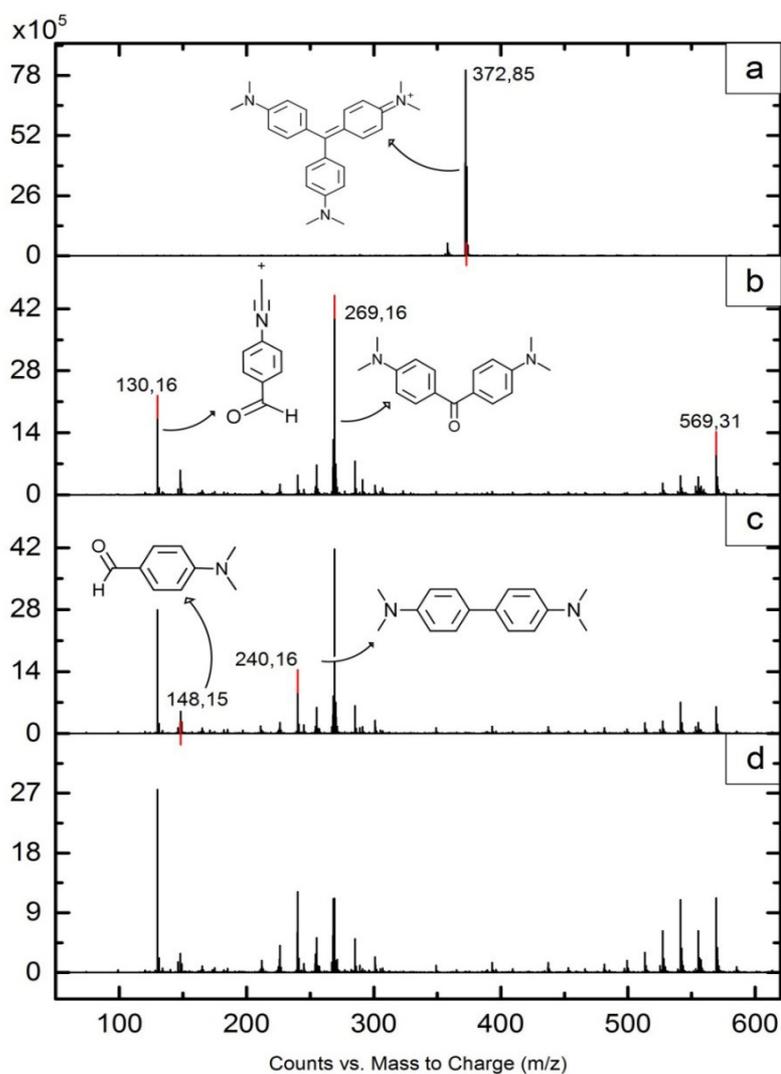
Figure 4. ESI mass spectra of CV (a) before degradation and after (b) 1 h, (c) 6 h, (d) 24 h of reaction time (reaction conditions: 5 mg catalyst, 25 mL 200 ppm CV solution, 13 µL H_2O_2, pH≤ 6, room temperature).

[28,29]. Nevertheless, the catalyst system is cost-effective, environmental-friendly and rapidly degrades CV into biodegradable products which itself is a resistant molecule to conventional biological wastewater treatment and biodegradation in natural environments [14].

Degradation of CV with $MnO_2@MnFe_2O_4$ Catalyst

Applying the same conditions given above for the layered MnO_2 catalyst, degradation of CV proceeded in a longer period with the $MnO_2@MnFe_2O_4$ catalyst. The catalytic reaction rate was relatively slow and complete decolorization of the dye solution was observed in ca. 4 hours due to the lower concentration of the active Mn sites present in

the shell for the same amount of the nanocomposite catalyst.

Magnetic nanocomposites have been used as recoverable, recyclable and efficient adsorbents for the removal of dye pollutants [30]. However, no such advantage is considered here for dye degradation reaction because the activity of the catalyst decayed eventually.

CONCLUSIONS

In the present study, degradation of aqueous CV dye solutions was studied comparatively with layered-MnO_2 and $MnO_2@MnFe_2O_4$ nanocompos-
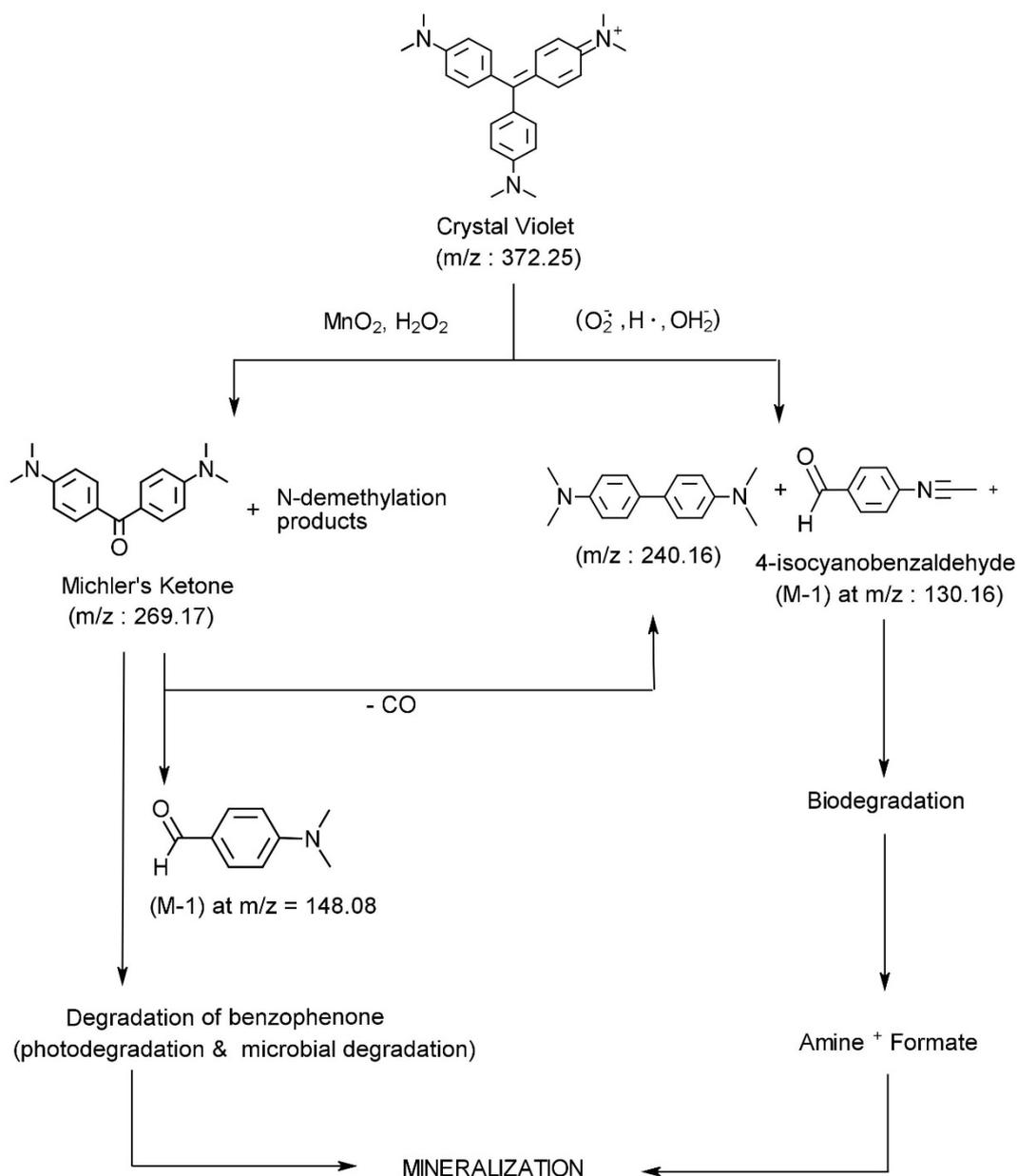
Scheme 2. Proposed degradation route for CV with MnO$_2$/H$_2$O$_2$ catalyst.

ite catalysts. The tests showed that both can degrade CV in the presence of H$_2$O$_2$ but the former with a higher activity. The degradation efficiency reached nearly 100% in 20 minutes when CV was degraded by layered-MnO$_2$.

The catalyst systems presented here are active with H$_2$O$_2$ which also causes a structural destruction of the catalyst eliminating the possibility of recycling. However, using a small amount of catalyst (5 mg) for a concentrated dye solution (ca. 200 ppm) might be considered as an advantage.

Degradation occurred through several different pathways as indicated by ESI-Q-ToF-MS analyses. Michler's ketone and 4-isocyanobenzaldehyde were proposed as main degradation products both of which can potentially be biodegraded to mineralization products. It is concluded that layered manganese oxides can be effectively applied in CV degradation reactions as cheap and environment friendly catalysts.

References

1. S. Dawood, T.K. Sen, Review on dye removal from its aqueous solution into alternative cost effective and non-conventional adsorbents, J. Chem. Process Eng., 1 (2013) 1.
2. S.G. Patel, N.R. Yadav, S.K. Patel, Evaluation of degradation characteristics of reactive dyes by UV/Fenton, UV/Fenton/activated charcoal, and UV/Fenton/TiO2 processes: A comparative study, Separ. Sci. Technol., 48 (2013) 1788-1800.
3. D. Vujevi, S. Papi, N. Koprivanac, A.L. Boži, Decolorization and mineralization of reactive dye by UV/Fenton process, Separ. Sci. Technol., 45 (2010) 1637-1643.
4. S. Atalay, G. Ersöz, Novel Catalysts in Advanced Oxidation of Organic Pollutants, SpringerBriefs in molecular science, Green Chemistry for Sustainability, Springer (2016).
5. K. Singh, S. Arora, Removal of synthetic textile dyes from wastewaters: a critical review on present treatment technologies, Crit. Rev. Env. Sci. Technol., 41 (2011) 807-878.
6. Z.-R. Tian, W. Tong, J.-Y. Wang, N.-G. Duan, V.V. Krishnan, S.L. Suib, Manganese oxide mesoporous structures: mixed-valent semiconducting catalysts, Science, 276 (1997) 926-930.
7. S.R. Segal, S.L. Suib, L. Foland, Decomposition of pinacyanol chloride dye using several manganese oxide catalysts, Chem. Mater., 9 (1997) 2526-2532.
8. T. Sriskandakumar, N. Opembe, C.-H. Chen, A. Morey, C. King'ondu, S.L. Suib, Green decomposition of organic dyes using octahedral molecular sieve manganese oxide catalysts, J. Phys. Chem. A, 113 (2009) 1523-1530.
9. N. Mittal, A. Shah, P.B. Punjabi, V. Sharma, Photodegradation of rose bengal using MnO2 (Manganese dioxide), Rasayan J. Chem, (2009) 516-520.
10. R. Kannan, A. Jegan, A. Ramasubbu, K. Karunakaran, S. Vasanthkumar, Synthesis and catalytic studies of layered and oms type nano manganese oxide material, J. Nanomater. Biostructure, 6 (2011) 755-760.
11. J. Ge, J. Qu, Degradation of azo dye acid red B on manganese dioxide in the absence and presence of ultrasonic irradiation, J. Hazard. Mater., 100 (2003) 197-207.
12. M.A. Al-Ghouti, Y.S. Al-Degs, M.A. Khraisheh, M.N. Ahmad, S.J. Allen, Mechanisms and chemistry of dye adsorption on manganese oxides-modified diatomite, J. Environ. Manage., 90 (2009) 3520-3527.
13. X. Li, S. Song, X. Wang, D. Liu, H. Zhang, Self-assembled 3D flower-like hierarchical Fe 3 O 4/K x MnO 2 core–shell architectures and their application for removal of dye pollutants, CrystEngComm, 14 (2012) 2866-2870.
14. S. Mani, R.N. Bharagava, Exposure to crystal violet, its toxic, genotoxic and carcinogenic effects on environment and its degradation and detoxification for environmental safety, Rev. Environ. Contam. Toxicol., 237, (2016), 71-104.
15. P. Rao, G. Patel, S. Sharma, S.C. Ameta, Photocatalytic degradation of crystal violet over semiconductor zinc oxide powder suspended in aqueous solution, Toxicol. Environ. Chem., 60 (1997) 155-161.
16. R. Ameta, J. Vardia, P.B. Punjabi, S.C. Ameta, Use of semiconducting iron (III) oxide in photocatalytic bleaching of some dyes, Indian J. Chem. Technol., 13,(2006) 114-118.
17. R. Ameta, D. Sharma, M. Ordia, Photocatalytic Degradation of Crystal Violet using Nickel Containing Polytungstometalate, Sci. Rev Chem. Commun., 3, (2013), 133-140.
18. P. Su, D. Chu, L. Wang, Studies on catalytic activity of nanostructure Mn2O3 prepared by solvent-thermal method on degrading crystal violet, Modern Appl. Sci., 4 (2010) 125.
19. I. Arslan-Alaton, B.H. Gursoy, J.E. Schmidt, Advanced oxidation of acid and reactive dyes: Effect of Fenton treatment on aerobic, anoxic and anaerobic processes, Dyes Pigm., 78 (2008) 117-130.
20. H.J. Fan, S.T. Huang, W.H. Chung, J.L. Jan, W.Y. Lin, C.C. Chen, Degradation pathways of crystal violet by Fenton and Fenton-like systems: condition optimization and intermediate separation and identification, J. Hazard. Mater., 171 (2009) 1032-1044.
21. G.Elmaci, C.E. Frey, P. Kurz, B. Zümreoğlu-Karan, Water Oxidation Catalysis by Birnessite@ Iron Oxide Core–Shell Nanocomposites, Inorg. Chem., 54 (2015) 2734-2741.
22. G. Elmacı, C.E. Frey, P. Kurz, B. Zümreoğlu-Karan, Water oxidation catalysis by using nano-manganese ferrite supported 1D-(tunnelled), 2D-(layered) and 3D-(spinel) manganese oxides, J. Mater. Chem. A, 4 (2016) 8812-8821.
23. R.J. Watts, J. Sarasa, F.J. Loge, A.L. Teel, Oxidative and reductive pathways in manganese-catalyzed Fenton's reactions, J. Environ. Eng., 131 (2005) 158-164.
24. S.H. Do, B. Batchelor, H.K. Lee, S.H. Kong, Hydrogen peroxide decomposition on manganese oxide (pyrolusite): kinetics, intermediates, and mechanism, Chemosphere, 75 (2009) 8-12.
25. D.Y. Chen, X.F. Guo, H. Wang, H.S. Zhang, The natural degradation of benzophenone at low concentration in aquatic environments, Water Sci. Technol., 72 (2015) 503-509.
26. M. Goda, Y. Hashimoto, S. Shimizu, M. Kobayashi, Discovery of a novel enzyme, isonitrile hydratase, involved in nitrogen-carbon triple bond cleavage, J. Biol. Chem., 276 (2001) 23480-23485.
27. H. Fukatsu, Y. Hashimoto, M. Goda, H. Higashibata, M. Kobayashi, Amine-synthesizing enzyme N-substituted formamide deformylase: screening, purification, characterization, and gene cloning, Proc. Natl. Acad. Sci. USA, 101 (2004) 13726-13731.
28. M. McBride, Oxidation of 1,2-and 1,4-dihydroxybenzene by birnessite in acidic aqueous suspension, Clays Clay Miner, 37 (1989) 479-486.
29. F. Schurz, J.M. Bauchert, T. Merker, T. Schleid, H. Hasse, R. Gläser, Octahedral molecular sieves of the type K-OMS-2 with different particle sizes and morphologies: Impact on the catalytic properties in the aerobic partial oxidation of benzyl alcohol, Appl. Catal. A, 355 (2009) 42-49.
30. R. Sivashankar, A. Sathya, K. Vasantharaj, V. Sivasubramanian, Magnetic composite an environmental super adsorbent for dye sequestration–A review, Environ. Nanotechnol. Monit. Manage., 1 (2014) 36-49.