



Chiang Mai J. Sci. 2018; 45(4) : 1901-1908
<http://epg.science.cmu.ac.th/ejournal/>
Contributed Paper

Synthesis and Characterization of Mechanochemically Synthesized Cobalt Oxide and Evaluation of its Catalytic Performance for Degradation of Congo Red Dye in Aqueous Medium

Mohsin Siddique* [a], Mohammad Ilyas [b, c] and Muhammad Saeed [d]

[a] Department of Chemistry, Bacha Khan University, Charsadda, Khyber Paktoonkhawa, Pakistan.

[b] National Centre of Excellence in Physical, Chemistry, University of Peshawar, Pakistan.

[c] Department of Chemistry, Qurtuba University of Science and Information Technology Peshawar Pakistan.

[d] Department of Chemistry, Government College University Faisalabad, Allama Iqbal Road Faisalabad Pakistan.

* Author for correspondence; e-mail: mohsin_phychem@bkuc.edu.pk

Received: 3 November 2016

Accepted: 18 March 2017

ABSTRACT

Catalytic oxidation/degradation of azo dye congo red (CR) was investigated at room temperature using lab synthesized cobalt oxide by a facile solid phase mechanochemical method. The catalyst was characterized by various techniques including X-Ray Diffraction (XRD), Fourier Transform Infrared (spectroscopy) (FT-IR), Scanning Electron Microscopy (SEM) and Surface area analysis. The catalyst showed excellent degradation ability in the presence of molecular oxygen and more than 85% of the dye was degraded in the first 10 minutes of the reaction at room temperature. It was observed that slight increase in the temperature enhances the degradation ability of the catalyst. The method of using cobalt oxide as catalyst shows many advantages including high degradation ratios, short reaction time, low cost; it may fit to deal with various other azo dyes in waste water on large scale.

Keywords: cobalt oxide, azo dyes, degradation, Congo red, oxidation

1. INTRODUCTION

Water pollution is a meaningful environmental headache created by discharge of textile effluent which contains intense coloured dye in large concentrations. The intense colour of these dyes is due to the existence of double bonds between two nitrogen atoms. These dyes containing textile effluents disturb the aqueous ecosystem either by destruction due to toxic nature or by

blocking the penetration of sunlight to the interior of water body [1-3]. The elimination of these dyes is important because many of these dyes are poisonous to the aquatic life. Many physical and chemical techniques including adsorption, membrane coagulation, ozonation, chemical oxidation, biochemical methods, biological degradation etc. have been employed for the removal of these dyes from

waste water streams [4-5]. Each of these mentioned techniques has some benefits and bad marks, however the catalytic decomposition of organic dyes is a very attractive efficient alternative for mineralization of dyes which converts the toxic dyes into harmless chemicals [6-7]. Cobalt oxide which is a non-precious metal oxide can be used a catalyst for a number of reactions. A number of factors affect the catalytic properties of cobalt oxide. The synthetic procedures, oxidation state of cobalt, surface structures, particles size distribution, surface area and morphology of the particles are various factors that affect the catalytic properties of cobalt oxide [8]. Tarka et al [9] have reported cerium and barium promoted cobalt oxide catalysts for synthesis of ammonia. It was noted that doubly promoted cobalt oxide with cerium and barium exhibit higher catalytic performance than singly promoted or simple non-promoted cobalt oxide. It confirmed that composition of catalyst is more important factor in catalytic activities of a catalyst. Iqbal and his co-workers [10] have reported the synthesis of carbon supported cobalt manganese oxide catalyst for Fischer Tropsch synthesis reaction. It was noted that carbon support and temperature treatment of the cobalt oxide greatly affect the catalytic activity and selectivity of the cobalt catalyst. Similarly, alumina, titania and silica supported cobalt oxide catalysts have been used for Fischer Tropsch synthesis reaction [11-12]. Similarly, other researchers have employed cobalt oxide catalyst for different reactions [13-17]. In present work we report degradation of CR dye catalysed cobalt oxide in aqueous medium in presence of molecular oxygen. CR is a diazole dye which is hard to be biodegraded and other treatments produces other types of pollutants; there is a need of such a technique which is cost effective, simple and does not produce toxic

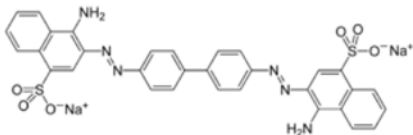
by-products. In this report, molecular oxygen was employed as an oxidant for degradation of CR dye. UV/Vis spectrophotometer was used to investigate the course of degradation of CR dye.

2. MATERIALS AND METHODS

2.1 Materials

Analytical grade chemicals were used in this study. CR dye was purchased from Sigma Aldrich. Table 1 lists the characteristics of CR. Cobalt nitrate (99 %) was supplied by Acros, USA. Ammonium bicarbonate (Laboratory grade) was supplied by Merck, Germany. Molecular oxygen (99% Pure) were supplied by BOC Pakistan limited. Triply distilled water was used for making dye solutions.

Table 1. Chemical properties of CR dye.


Chemical Structure of Congo red Dye
Chemical Formula: $C_{32}H_{22}N_6Na_2O_6S_2$
Molar Mass: $669.66 \text{ g mol}^{-1}$

2.2 Catalyst Preparation

Cobalt oxide catalyst was synthesized using solid state route [8]. Typically, cobalt nitrate and ammonium bicarbonate was taken in a fixed molar ratio i.e. 2:5 respectively. The two salts were thoroughly mixed and grinded in solid phase continuously for one hour. The reaction resulted in a homogeneous paste. The paste was aged for 24 hours so that the unreacted salts if any get reacted. The resultant paste was dried overnight at 383 K. The dried powder was converted into fine powder and was washed several times

with triply distilled water. The black powder was dried and then calcined at 573 K for 4 hours.

2.3 Catalyst Characterization

For determination of surface area of cobalt oxide by nitrogen adsorption Quanta Chrome surface area analyser was used. Prior to nitrogen adsorption at 77 K, the catalysts sample was degassed at 423 K. For estimation of particle size distribution of cobalt oxide by wet method of analysis, Analysette 22 Compact was used. For estimation of crystalline nature of cobalt oxide, JEOL X-Ray Diffractometer (JDX-3532) was employed. Infrared spectra of the catalysts were recorded with IR-Prestige 21, Shimadzu in KBr medium. JEOL JSM-5910 was used for scanning electron microscopy of the catalyst samples.

2.4 Reaction Protocols

Three-necked flask (100 mL) provided with condenser, thermometer and inlet for oxygen/nitrogen was used as batch reactor and hot plate as source of temperature. Degradation experiments of CR dye over cobalt oxide catalyst were performed at different temperatures (303, 308 and 313 K) at pH 6 to 7 using 50 mgL^{-1} as initial concentration of dye under continuous flow of oxygen at 1 atm pressure. In a typical experiment, the reactor was loaded with dye solution (50 mL) and was stirred under the flow of oxygen at a specified temperature for 30 minutes. After stirring period, 1 mL sample was taken to determine any change in the CR concentration during the heating period. Then 30 mg of cobalt oxide catalyst was added followed by stirring of reaction mixture. After each 15 minutes of interval, samples from reaction mixture were taken

and analysed with double beam UV/Vis spectrophotometer (UV-160A Shimadzu). Following equation was used to calculate the percent degradation of dye.

$$\text{Degradation (\%)} = \frac{(\text{dye})_0 - (\text{dye})_t}{(\text{dye})_0} (\times) 100 \quad (1)$$

Where $(\text{dye})_0$ is the initial concentration and $(\text{dye})_t$ is concentration of dye at various time.

3. RESULTS AND DISCUSSIONS

3.1 Characterization

The BET surface area of cobalt oxide was found as $73 \text{ m}^2/\text{g}$. The mean pore radius was approximately equal to 4.5 nm. The pore size distribution show that 90% of the pores are $\geq 4.5 \text{ nm}$. The particle size of the powder was found to be equal 3-10 micrometer using laser light scattering method. The XRD patterns of the catalyst can be shown in Figure 1. The pattern shows the crystalline nature of cobalt oxide having various peaks. Peaks at 31.2, 36.8, 45.5 and 59.1 2θ degree are assigned to (2 2 0), (3 1 1), (4 0 0) and (5 1 1) lattices of cobalt oxide respectively [8, 18, 19].

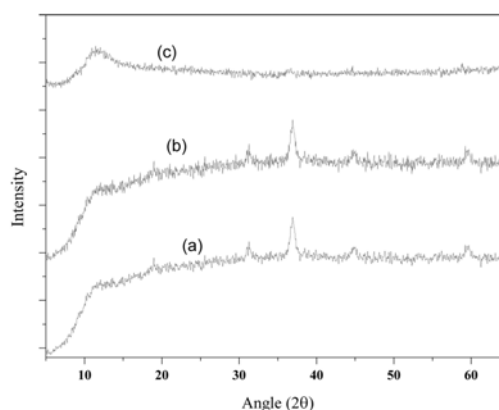


Figure 1. XRD Pattern of (a) Fresh, (b) Used in oxygen atmosphere, (c) Used in nitrogen atmosphere.

The XRD patterns of the (a) Fresh (b) used in oxygen and (c) used in inert atmosphere of molecular nitrogen, suggests that there is no difference between (a) and (b) which shows that the degradation process has occurred on the catalyst surface. However, the catalyst used in the inert atmosphere i.e (c) is different from (a) and (b) suggests that the dye has merely adsorbed on the surface of the catalyst, and no degradation of the dye has occurred. Hence the presence of oxygen is vital for the degradation process of the dye.

The SEM images of the catalyst are shown in Figure 2 which suggest the particles are in range of 5-10 micron meter in size. It can also be noted that there is no major difference in morphology of fresh and used catalyst samples. However, the used catalyst seems to be scuffed off which suggests the adsorption of reactants/products at the surface of catalysts. Surface of catalyst restores after calcination.

The IR spectra of the catalyst used in different reaction conditions are shown in Figure 3. There seems no difference between the fresh (a) and the catalyst used in presence of oxygen which confirms our earlier conclusion drawn in the discussion of XRD that CR dye has degraded and the catalyst surface is regenerated again, however, the IR spectra of the catalyst used in nitrogen atmosphere is different from both (a) and (b) which suggests that adsorption of the dye has occurred on the catalyst surface. The bands present between 3200-3500 cm^{-1} and at 1600 cm^{-1} is due to the water on the catalyst surface. Peaks present at 660 cm^{-1} and 570 cm^{-1} are assigned to spinal for of Co_3O_4 [8]. In spectrum c some additional peaks were observed which indicate the adsorption of CR dye on surface of cobalt oxide. Peak at 3306 cm^{-1} is due to stretching vibration of N-H. Another peak at 1550 cm^{-1} indicates

N=N (azo) stretching, and the peak at 1175 cm^{-1} indicates the $-\text{SO}_3^-$ stretching [20].

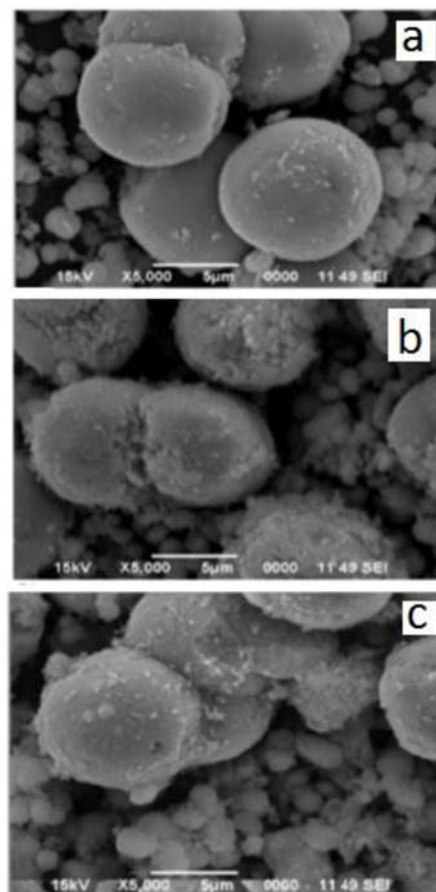


Figure 2. SEM images of (a) Fresh, (b) Used in oxygen and (c) Used in nitrogen atmosphere.

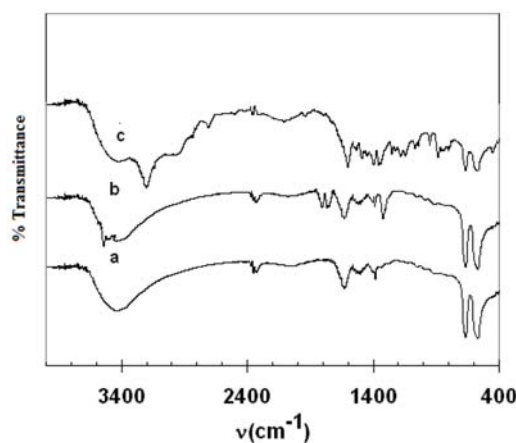


Figure 3. IR Spectra of (a) Fresh (b) Used in oxygen and (c) Used in nitrogen atmosphere.

3.2 Comparison of Different Catalysts

Catalytic activity of cobalt oxide for degradation of CR dye was compared with oxides of iron, nickel and manganese. Commercial grade oxides of iron, nickel and manganese were used for comparison.

It was observed that cobalt oxide was more effective catalyst for degradation of CR dye in present study. Degradation of dye achieved in 90 minutes at room temperature with different catalysts are given in Table 2.

Table 2. Degradation of Congo Red with different catalysts.

S/No	Catalyst Name	Decolonization %	Reaction Time (mins)	Reaction temperature (K)
1	Nickel oxide	63	90	303
2	Iron Oxide	52	90	303
3	Manganese oxide	79	90	303
4	Cobalt Oxide	96	90	303

3.3 Time Profile

Degradation of CR dye over cobalt oxide catalyst is given Figure 4(a). From the data, it can be concluded that present cobalt oxide is highly active catalyst. It was observed that 80% degraded within 30 minutes of reaction time at 298 K. After 90 minutes of reaction time, 96% dye was degraded. At 313 K, 99% dye degraded in 90 minutes. Hence, it can be concluded that lab prepared cobalt oxide can be used as effective catalyst for degradation of CR dye. Figure 4(b) showing the decolourization of the dye with respect time. Formation of electron-hole pair between valence and conduction band of cobalt oxide is the proposed mechanism in present study. Adsorbed O_2 at the surface of catalysts scavenges the electron and result in formation of superoxide anion (O_2^-) which produce OOH radicals by protonation. The hole produce active OH radicals by reaction with water. The active radicals take part in degradation of CR dye. Decomposition of the dye molecule takes place at various points leading to formation of various intermediate

products. Degradation of CR dye may take place via cleavage of C-S bond between sulfonate group and aromatic ring by hydroxyl radicals, cleavage on -N=N- bond, ring opening, cleavage of C-N and C-C bonds and decarboxylation by reaction with OH radicals. FTIR suggests the existence of some products. Bands at 1334, 1730 and 3445 cm^{-1} are attributed to degradation products NO_3^{-1} , COO^{-1} and $-NH_2$ respectively [3, 5, 21-23].

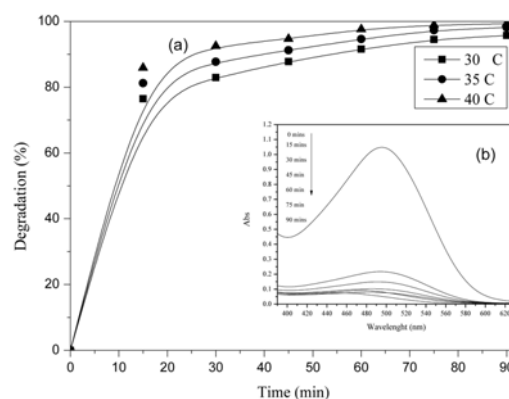


Figure 4. The dye removal of Congo red with time, pH 6-7 (b) UV/Vis spectra of Congo Red Degradation at different times.

3.4 Effect of Catalyst Loading

The addition of catalyst is an important parameter in treating waste water in photocatalytic, sono catalytic and other catalytic degradation processes. The consequences of catalyst dose on degradation of CR dye was studied over various catalyst doses in the range of 10-100 mg under identical experimental conditions. It was noted that degradation of dye increases linearly with catalyst dose up to 70 mg of catalyst dose and there was no effect of catalyst dose above 70 mg as given in Figure 5. Degradation behaviour of CR dye in present study below 70 mg of catalyst dose suggests mass-transport-limitation of dye to the surface of catalyst [24]. Similarly, the effect of temperature on degradation of CR dye under identical condition was also investigated. With temperature degradation of dye increases as given in Figure 6. Activation energy was calculated as 11.1 kJmol^{-1} .

The effect of partial pressure of oxygen on degradation of CR dye over cobalt oxide was investigated in the range of 17 - 101 kPa under identical conditions. Results are given in Figure 7. It is evident that with the increase of partial pressure of oxygen the rate of degradation of the dye increases, reaching 99% activity at 101 kPa in 90 minutes.

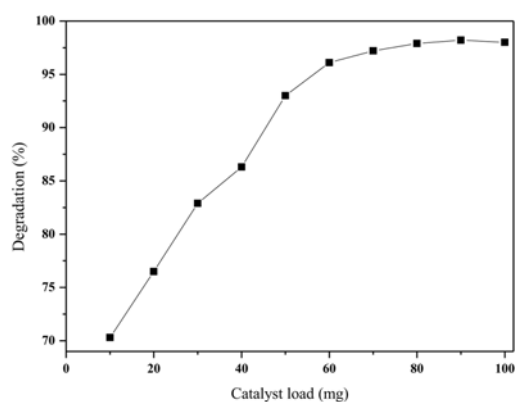


Figure 5. Effect of catalyst loading on the degradation of dye at 303K.

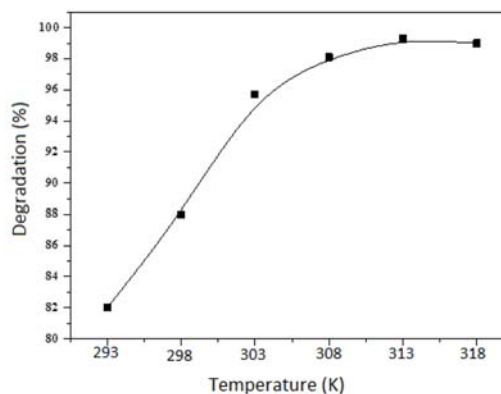


Figure 6. Effect of temperature on the degradation of CR-Dye.

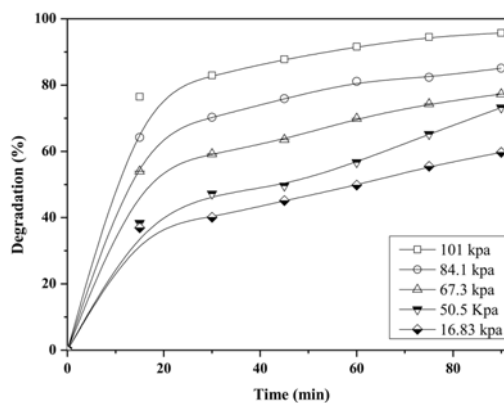


Figure 7. Effect of partial pressure of oxygen on the degradation of CR dye at 303 K.

3.5 Life Span of the Catalyst

To check the possible re-usability of cobalt oxide, the spent catalyst was re-used for degradation of CR dye under identical experimental conditions. Spent catalyst was recycled 5 times and it was noted that there was a small loss in catalytic activity of cobalt oxide in degradation experiments. In another experiment, the spent catalyst was washed with ethanol and water followed by calcination at 573 K and was employed as catalyst for degradation of dye. It was noted that this catalyst exhibited the same activity as fresh cobalt oxide. Washing removes the adsorbed species therefore catalytic is regenerated. The comparison is shown in the following Figure 8.

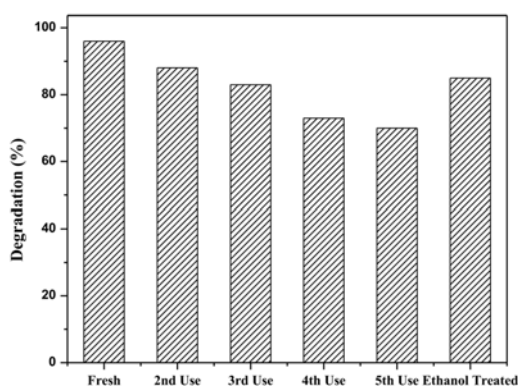


Figure 8. Life span of catalyst at 303K.

4. CONCLUSIONS

It can be concluded that Co_3O_4 prepared by mechanochemical method can be used as an effective catalyst for degradation of CR dye at ambient temperature and pressure. Cobalt oxide is heterogeneous in nature in present study which can be separated from reaction mixture by simple filtration. More than 90% of dye degraded within 30 minutes of time. Moreover, the efficiency of the catalyst is good enough to be used for longer periods of time and the degradation of the dye decreases with the decrease of oxygen contents in the reaction mixture. Formation of electron-hole pair between valence and conduction band of cobalt oxide is the proposed mechanism in present study.

REFERENCES

- [1] Khan A., Rehman Z., Rehman M., Khan R., Zulfiqar, Waseem A. and Iqbal A., *Inorg. Chem. Commun.*, 2016; **72**: 33-41. DOI 10.1016/j.inoche.2016.08.001.
- [2] Ajmal A., Majeed I., Malik R.N., Idriss H. and Nadeem M.A., *RSC Adv.*, 2014; **4**: 37003-37026. DOI 10.1039/C4RA06658H.
- [3] Saeed M., Jamal M.A., Haq A., Ilyas M., Younas M. and Shahzad M.A., *Int. J. Chem. React. Eng.*, 2016; **24**: 45-51. DOI 10.1515/ijcre-2015-0088.
- [4] Vandeviere P.C., Bianchi R. and Verstrate W., *J. Chem. Technol. Biotechnol.*, 1998; **72**: 289-302. DOI 10.1002/(SICI)1097-4660(199808)72:4<289::AID-JCTB905>3.0.CO2-#.
- [5] Saeed M., Adeel S., Ilyas M., Shahzad M.A., Usman M., Haq E. and Hamayun M., *Desal. Water Treatment*, 2016; **57**: 12804-12813. DOI 10.1080/19443994.2015.1052992.
- [6] Tanwar R., Kumar S. and Mandal U.K., *J. Photochem. Photobiol. A: Chem.*, 2017; **333**: 105-116. DOI 10.1016/j.jphotochem.2016.10.022.
- [7] Andreozzi R., Caprio V., Insola A. and Marotta R., *Catal. Today*, 1999; **53**: 51-59. DOI 10.1016/S0920-5861(99)00102-9.
- [8] Ilyas M. and Saeed M., *Int. J. Chem. React. Eng.*, 2010; **8**: A77.
- [9] Tarka A., Zybert M., Kindler Z., Szmurlo J., Mierzwa B. and Pilecka W.R., *Appl. Catal. A Gen.*, 2017; **532**: 19-32. DOI 10.1016/j.apcata.2016.11.030.
- [10] Iqbal S., Davies T.E., Morgan D.J., Karim K., Hayward J.S., Bartley J.K., Taylor S.H. and Hutchings G.J., *Catal. Today*, 2016; **275**: 35-39. DOI 10.1016/j.cattod.2015.09.041.
- [11] Pendyala V.R., Jacob G., Bertaux C., Khalid S. and Davis B.H., *J. Catal.*, 2016; **337**: 80-90. DOI 10.1016/j.jcat.2016.01.026.
- [12] Jacob G., Bertaux C., Pendyala V.R., Shafer W.D., Poirier J.S., Xiao Q., Hu Y. and Davis B.H., *Appl. Catal. A Gen.*, 2016; **516**: 51-57. DOI 10.1016/j.apcata.2016.02.017.
- [13] Behling R., Chatel G. and Valange S., *Ultra. Sonochem.*, 2017; **36**: 27-35. DOI 10.1016/j.ultsonch.2016.11.015.

- [14] Bialas A., Mazur M., Natkanski P., Dudek B., Kozak M., Wach A. and Kustrowski P., *Appl. Surf. Sci.*, 2016; **362**: 297-303. DOI 10.1016/j.apsusc.2015.11.211.
- [15] Wang Z. and Spivey J.J., *Appl. Catal. A Gen.*, 2015; **507**: 75-81. DOI 10.1016/j.apcata.2015.09.032.
- [16] Wang P., Chen S., Bai Y., Gao X., Li X., Sun K., Xie H., Yang G., Han Y. and Tan Y., *Fuel*, 2017; **195**: 69-81. DOI 10.1016/j.fuel.2017.01.050.
- [17] Mukhopadhyay P. and Chakraborty R., *Catal. Commun.*, 2017; **95**: 73-76. DOI 10.1016/j.catcom.2017.02.020.
- [18] Bulavchenko O.A., Cherepanova S.V., Malakhov V.V., Dovlitova L.S., Ishchenko A.V. and Tsybulya S.V., *Kin. Catal.*, 2009; **50**: 192-198. DOI 10.1134/S0023158409020086.
- [19] Glaspell G.P., Jadodzinski P.W. and Manivannan A., *J. Phys. Chem. B*, 2004; **108**: 9604-9607. DOI 10.1021/jp0370831.
- [20] Chawla S., Uppal H., Yadav M., Bahadur N. and Singh N., *Ecotoxicol. Environ. Safety*, 2017; **135**: 68-74. DOI 10.1016/j.ecoenv.2016.09.017.
- [21] Huang F., Chen L., Wang H. and Yan Z., *Chem. Eng. J.*, 2010; **162**: 250-256.
- [22] Chen G., Si X., Yu J., Bai H. and Zhang X., *Appl. Surf. Sci.*, 2015; **330**: 191-199. DOI 10.1016/j.apsusc.2015.01.011.
- [23] Jamal A., Rahman M.M., Khan S.B., Faisal M., Akhtar K., Rub M.A., Asiri A.M. and Al-Youbi A.O., *Appl. Surf. Sci.*, 2012; **261**: 52-58. DOI 10.1016/j.apsusc.2012.07.066.
- [24] Saeed M., Siddique M., Usman M., Haq A., Kham S.G. and Raouf H.A., *Z. Phys. Chem.*, 2017; **231**. DOI 10.1515/zpch-2016-0921.