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DEGRADATION OF REACTIVE BLACK 5 FROM AQUEOUS EFFLUENTS USING OZONE AND NiO/Al_2O_3 CATALYSTS

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The aim of this study was to synthesize and evaluate NiO/Al_2O_3 catalysts for their efficiency in the advanced oxidation process (AOP) applied to the removal of Reactive Black 5 (RB5) dye from aqueous solutions. Ozone was employed as the oxidizing agent, both alone and in combination with the prepared catalysts, to assess their synergistic effect on pollutant degradation.

The experimental results demonstrated that the presence of NiO/Al_2O_3 catalysts significantly enhanced both the decolorization of RB5 and the overall mineralization of organic compounds, compared to ozonation alone. Among the tested conditions, the optimal catalyst dosage was determined to be 2 g/L, providing the most effective balance between catalytic activity and operational efficiency.

These findings highlight the potential of NiO/Al_2O_3 catalysts as promising materials for catalytic ozonation in wastewater treatment applications.

Keywords: ozone, advanced oxidation processes, catalysts, total organic carbon

1. Introduction

The presence, even of small concentrations of pigments, in aqueous effluents is very visible and unwanted, because the introduction of colored water into the ecosystem involves aesthetic pollution and environmental problems such as disturbance of aquatic life, reduction of biodiversity affecting photosynthesis processes [1]. There are over 100,000 commercially available dyes and over 7 x 10^5 tons are produced annually. Dyes are not completely bound in the factory and depending on the type of dye they are lost in the wastewater: 2% in for basic dyes and over 50% for reactive dyes, causing serious environmental problems. In 2023, between 120 - 140 thousand tons of dyes were produced worldwide [2-4]. During the dyeing process, only 50 - 90% of the dye binds to the fiber, the rest hydrolyzes and is eliminated in the environment by washing [5-8]. For example, to treat one kg of cotton fibers, between 80 and 100 L of water are required, thus generating huge quantities of colored water. This water cannot be reused, cannot be discharged to the sewage system, nor can it be released into the environment without prior

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treatment. Azo dyes (chromophore group: -N = N-) are among the most widely used dyes in the dyeing process in the textile industry; but they are also used in the cosmetics industry, the paper and photographic industry, tanning processes etc.

Dyes generally have complex aromatic structures and high stability in solution, therefore, conventional biological treatment methods and activated sludge processes are ineffective in bleaching processes. Some azo dyes give carcinogenic reaction by-products [9-11]. Treatment processes such as coagulation/flocculation, reverse osmosis and adsorption have the disadvantage of transferring the pollutant to another environment leading to secondary pollution. New wastewater treatment technologies, which ensure a complete mineralization of organic pollutants, are currently considered the most appropriate solution, given the drastic requirements regarding the level of wastewater contamination. One of the major directions in which water treatment technologies are evolving is the development of new extensive oxidation processes [12-21]. These methods are based on the activation of powerful oxidizing agents, like ozone and/or hydrogen peroxide, with the generation of radical species with high redox potential. Catalytic processes can be considered an alternative for the purification of dyes from wastewater.

Recent studies have demonstrated that the photocatalytic process can be used for the mineralization of organic compounds or the degradation of dyes using TiO2 in the presence of UV radiation. Photocatalytic processes do not require expensive oxidants and can take place at normal temperature and pressure, this being the main advantage compared to other oxidation processes.

The azo dyes, characterized by an azo group (-N=N-), represent a comprehensive category of dyes employed in textile industry for dyeing of a large category of materials [18, 21-23]. Different types of azo dyes are synthesized in industry (acid, reactive, disperse, vat, metal complex, mordant, direct, basic and sulphur) but the reactive type are largely used and represent a significant threat for aqueous environment since more than 16% of these compounds can be found in industrial wastewaters. In this study Reactive Black 5 (RB5) was used as azo dye model compound to mimic the water pollution and the purification process using catalysts and ozone as a tandem for advanced putrification. The catalytic system used for this process was NiO supported on alumina and was obtained by impregnation followed by calcination at 550 °C

2. Materials and methods

The catalyst was prepared by immersing Al_2O_3 pellets in aqueous solutions of nickel nitrate. Concentration of nickel solution and Al_2O_3 amount were calculate in order to obtain a concentration 10% metal in the solid catalyst. After the impregnation process, the solid precursors were dried at 120°C for 4 hours and calcined at 550°C for 4 hours (Fig. 2). Oxidation tests were performed in a semi - batch reactor (Fig. 3).

Experimental conditions:

- Gas flow: 20 L h^{-1}
- Solution volume: 800 ml
- RB concentration: 500 mg/l
- Temperature: 22 ± 0.5 °C
- pH_i= 2.4; 5.4; 10.5
- Catalyst dose: 1; 2; 4 g/L
- Ozone addition rate: 6.5 mg min^{-1}

NiO/Al_2O_3 catalyst:

S_{BET} = 203.1

Phase composition: NiO; η(γ)–Al2O3

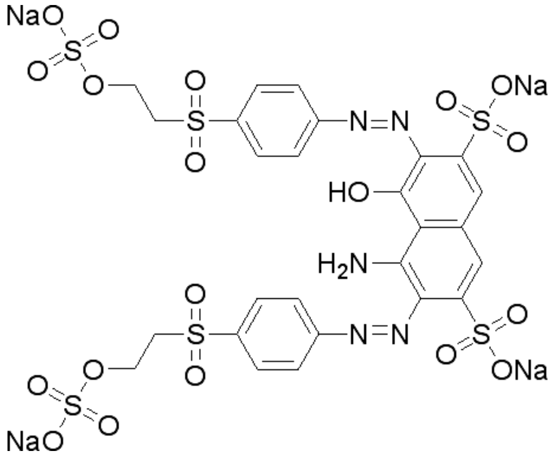

Fig. 1. Structure of Reactive Black 5 (RB5)

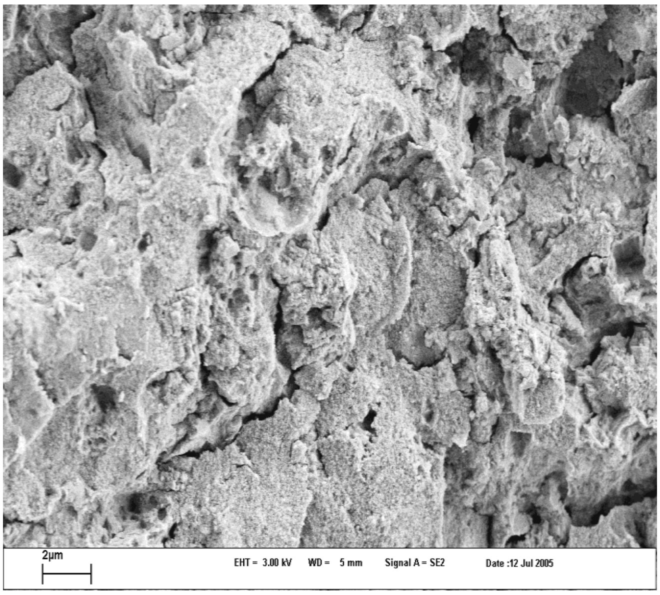

Fig. 2. SEM image for prepared catalyst.

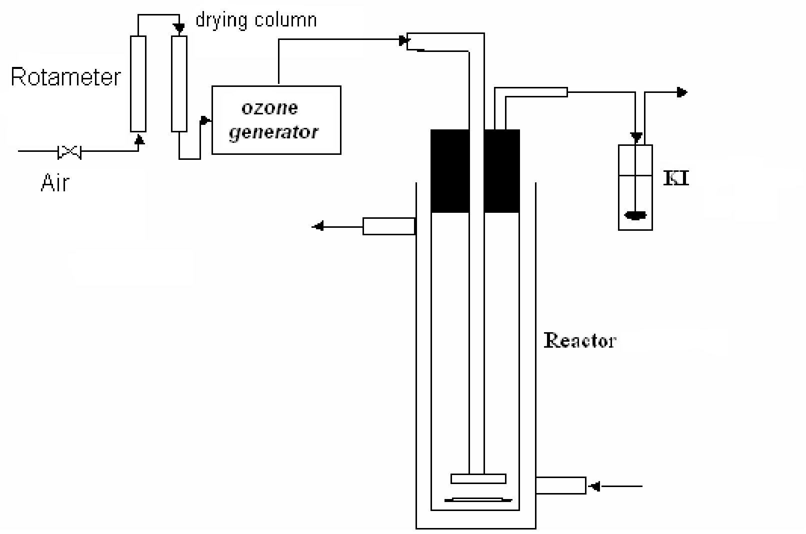

Fig. 3. Experimental set-up used in the ozonization process

3. Results and Discussions

Experimental tests have proven that the ozonation process is very efficient for destruction of chromophore group of RB5 and with the help of prepared catalyst the reaction rate increase significantly (Fig. 4). However, the removal of TOC during the oxidation process is considerable slower especially in absence of catalyst (up to 120 minutes for catalytic process) (Fig. 5).

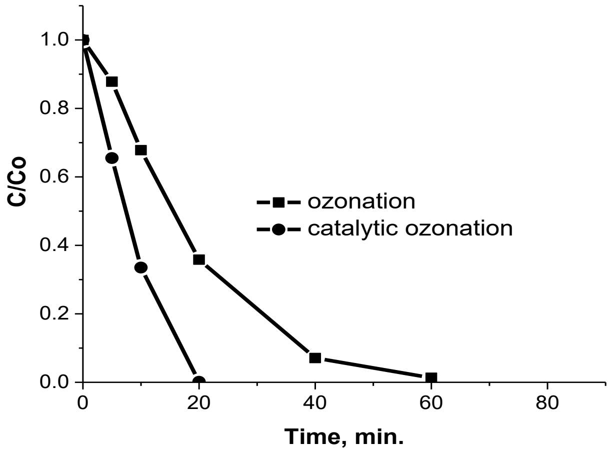

Fig. 4. Evolution of RB5 concentration in the ozonation process for NiO/Al$_2$O$_3$ catalyst

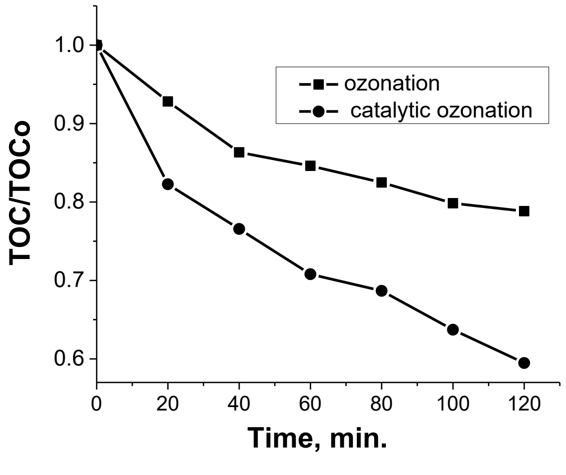

Fig. 5. Evolution of TOC in the ozonation process for NiO/Al$_2$O$_3$ catalyst

The pH of solution at the beginning of reaction has a considerable influence on the reaction rate both in terms of color removal and TOC removal. Thus, for acid pH reaction rate is much slower comparative with experiments performed on neutral and basic pH (Fig. 6).

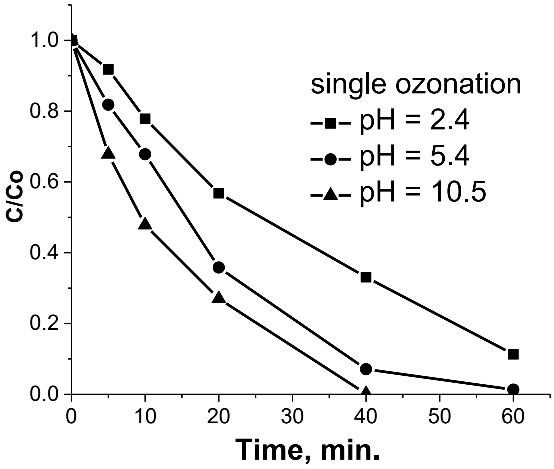

Fig. 6. Influence of pH on RB removal for single ozonation

In the case of catalytic process, the removal of RB5 occur almost the same for a large pH domain (Fig. 7).

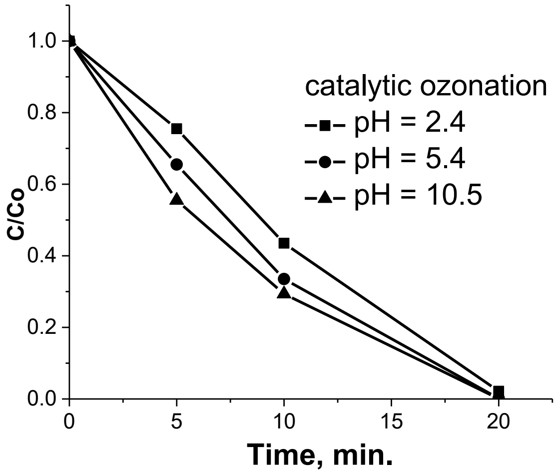

Fig. 7. Influence of pH on RB5 removal for catalytic ozonation process

TOC removal rate strongly decreases for acidic media in absence of catalyst compared with catalytic processes (Fig. 8, 9).

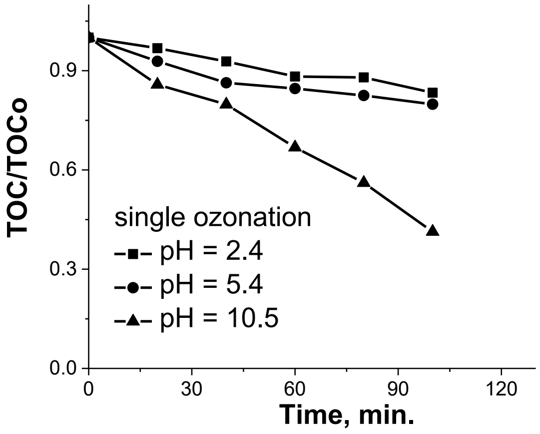

Fig. 8. Variation of TOC in the ozonation process in absence of catalysts

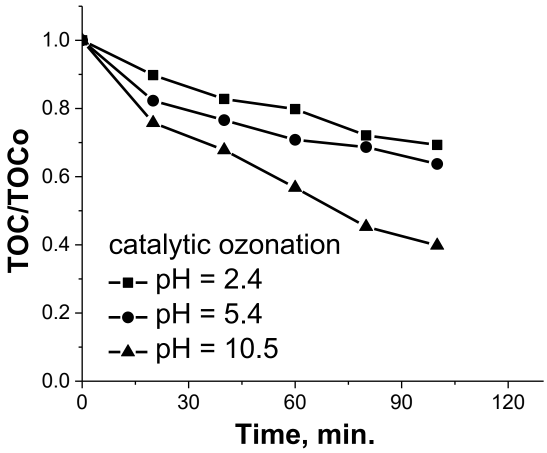

Fig. 9. Variation of TOC in the catalytic ozonation process

This behavior can be assigned to hydroxyl radicals production in the presence of studied catalyst even at lower values of pH. Increasing the catalyst dose lead to an increase of reaction rate but after a concentration of 2g/L the removal of RB becomes comparable whit 4 g/L dose thus it can be considered that optimal dose for this process is 2g/L (Fig. 10).

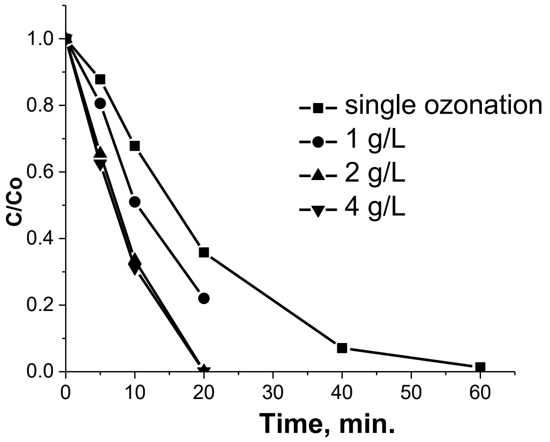

Fig. 10. Influence of catalyst dose on RB5 removal

4. Conclusions

The application of NiO/Al_2O_3 catalysts in the catalytic ozonation process significantly enhances the removal efficiency of Reactive Black 5 from aqueous solutions compared to non-catalytic ozonation. The presence of the catalyst not only accelerates the degradation rate of the dye but also promotes a higher degree of mineralization of the organic content. The study revealed that both the pH of the solution, within the range of 2 to 11, and the catalyst dosage positively influence the reaction kinetics.

An optimal catalyst dose of 2 g/L was identified, at which complete removal of the dye was achieved. Increasing the catalyst dosage beyond this value did not result in a substantial improvement in the oxidation performance, indicating that 2 g/L represents an efficient and cost-effective threshold for treatment. These findings demonstrate the potential of NiO/Al_2O_3 catalysts to serve as effective agents in advanced wastewater treatment technologies aimed at the removal of persistent organic pollutants.

REFERENCES

[1] A. Tkaczyk, K. Mitrowska, and A. Posyniak, “Synthetic organic dyes as contaminants of the aquatic environment and their implications for ecosystems: A review,” Science of The Total Environment, vol. 717, pp. 137222, 2020/05/15/, 2020.

[2] M. Usman, A. Ahmed, B. Yu, S. Wang, Y. Shen, and H. Cong, “Simultaneous adsorption of heavy metals and organic dyes by β-Cyclodextrin-Chitosan based cross-linked adsorbent,” Carbohydrate Polymers, vol. 255, pp. 117486, 2021/03/01/, 2021.

[3] A. Velidandi, N. P. P. Pabbathi, and R. R. Baadhe, “Study of parameters affecting the degradation of rhodamine-B and methyl orange dyes by Annona muricata leaf extract

synthesized nanoparticles as well as their recyclability," Journal of Molecular Structure, vol. 1236, pp. 130287, 2021/07/15/, 2021.

[4] R. Vidhya, R. Gandhimathi, R. Karthikeyan, and K. Neyvasagam, "Visible light driven enhancement in photodegradation of organic dyes using FexTi1-xO2 thin films," Materials Today: Proceedings, vol. 47, pp. 1819-1828, 2021/01/01/, 2021.

[5] M. M. H. El-Sayed, R. E. Elsayed, A. Attia, H. H. Farghal, R. A. Azzam, and T. M. Madkour, "Novel nanoporous membranes of bio-based cellulose acetate, poly(lactic acid) and biodegradable polyurethane in-situ impregnated with catalytic cobalt nanoparticles for the removal of Methylene Blue and Congo Red dyes from wastewater," Carbohydrate Polymer Technologies and Applications, vol. 2, pp. 100123, 2021/12/25/, 2021.

[6] M. Essandoh, R. A. Garcia, V. L. Palochik, M. R. Gayle, and C. Liang, "Simultaneous adsorption of acidic and basic dyes onto magnetized polypeptidylated-Hb composites," Separation and Purification Technology, vol. 255, pp. 117701, 2021/01/15/, 2021.

[7] S. Feng, and F. Li, "Photocatalytic dyes degradation on suspended and cement paste immobilized TiO2/g-C3N4 under simulated solar light," Journal of Environmental Chemical Engineering, vol. 9, no. 4, pp. 105488, 2021/08/01/, 2021.

[8] C. Huang, H. Liao, X. Ma, M. Xiao, X. Liu, S. Gong, X. Shu, and X. Zhou, "Adsorption performance of chitosan Schiff base towards anionic dyes: Electrostatic interaction effects," Chemical Physics Letters, vol. 780, pp. 138958, 2021/10/01/, 2021.

[9] E. Akceylan, M. Bahadir, and M. Yılmaz, "Removal efficiency of a calix[4]arene-based polymer for water-soluble carcinogenic direct azo dyes and aromatic amines," Journal of Hazardous Materials, vol. 162, no. 2, pp. 960-966, 2009/03/15/, 2009.

[10] T. N. J. I. Edison, R. Atchudan, M. G. Sethuraman, and Y. R. Lee, "Reductive-degradation of carcinogenic azo dyes using Anacardium occidentale testa derived silver nanoparticles," Journal of Photochemistry and Photobiology B: Biology, vol. 162, pp. 604-610, 2016/09/01/, 2016.

[11] S. Shahabuddin, R. Khanam, M. Khalid, N. M. Sarih, J. J. Ching, S. Mohamad, and R. Saidur, "Synthesis of 2D boron nitride doped polyaniline hybrid nanocomposites for photocatalytic degradation of carcinogenic dyes from aqueous solution," Arabian Journal of Chemistry, vol. 11, no. 6, pp. 1000-1016, 2018/09/01/, 2018.

[12] I. Arslan-Alaton, B. H. Gursoy, and J.-E. Schmidt, "Advanced oxidation of acid and reactive dyes: Effect of Fenton treatment on aerobic, anoxic and anaerobic processes," Dyes and Pigments, vol. 78, no. 2, pp. 117-130, 2008/08/01/, 2008.

[13] A. P. Bhat, and P. R. Gogate, "Degradation of nitrogen-containing hazardous compounds using advanced oxidation processes: A review on aliphatic and aromatic amines, dyes, and pesticides," Journal of Hazardous Materials, vol. 403, pp. 123657, 2021/02/05/, 2021.

[14] U. B. Deshannavar, P. Kumar Singa, D. Gaonkar, A. Gayathri, A. Patil, and L. V. Malade, "Removal of Acid Violet 49 and Acid Red 88 dyes from Aqueous Solutions using Advanced Oxidation Process," Materials Today: Proceedings, vol. 24, pp. 1011-1019, 2020/01/01/, 2020.

[15] M. Faouzi, P. Cañizares, A. Gadri, J. Lobato, B. Nasr, R. Paz, M. A. Rodrigo, and C. Saez, "Advanced oxidation processes for the treatment of wastes polluted with azoic dyes," Electrochimica Acta, vol. 52, no. 1, pp. 325-331, 2006/10/05/, 2006.

[16] V. Javanbakht, and M. Mohammadian, "Photo-assisted advanced oxidation processes for efficient removal of anionic and cationic dyes using Bentonite/TiO2 nano-photocatalyst

immobilized with silver nanoparticles," Journal of Molecular Structure, vol. 1239, pp. 130496, 2021/09/05/, 2021.

[17] Y.-G. Kang, H. Yoon, C.-S. Lee, E.-J. Kim, and Y.-S. Chang, "Advanced oxidation and adsorptive bubble separation of dyes using MnO2-coated Fe3O4 nanocomposite," Water Research, vol. 151, pp. 413-422, 2019/03/15/, 2019.

[18] F. Medrano-Rodríguez, A. Picos-Benítez, E. Brillas, E. R. Bandala, T. Pérez, and J. M. Peralta-Hernández, "Electrochemical advanced oxidation discoloration and removal of three brown diazo dyes used in the tannery industry," Journal of Electroanalytical Chemistry, vol. 873, pp. 114360, 2020/09/15/, 2020.

[19] A. Muniyasamy, G. Sivaporul, A. Gopinath, R. Lakshmanan, A. Altaee, A. Achary, and P. Velayudhaperumal Chellam, "Process development for the degradation of textile azo dyes (mono-, di-, poly-) by advanced oxidation process - Ozonation: Experimental & partial derivative modelling approach," Journal of Environmental Management, vol. 265, pp. 110397, 2020/07/01/, 2020.

[20] P. V. Nidheesh, M. Zhou, and M. A. Oturan, "An overview on the removal of synthetic dyes from water by electrochemical advanced oxidation processes," Chemosphere, vol. 197, pp. 210-227, 2018/04/01/, 2018.

[21] A. Khataee, A. Fazli, F. Zakeri, and S. W. Joo, "Synthesis of a high-performance Z-scheme 2D/2D WO3@CoFe-LDH nanocomposite for the synchronic degradation of the mixture azo dyes by sonocatalytic ozonation process," Journal of Industrial and Engineering Chemistry, vol. 89, pp. 301-315, 2020/09/25/, 2020.

[22] Z. U. H. Khan, A. Khan, Y. Chen, A. u. Khan, N. S. Shah, N. Muhammad, B. Murtaza, K. Tahir, F. U. Khan, and P. Wan, "Photo catalytic applications of gold nanoparticles synthesized by green route and electrochemical degradation of phenolic Azo dyes using AuNPs/GC as modified paste electrode," Journal of Alloys and Compounds, vol. 725, pp. 869-876, 2017/11/25/, 2017.

[23] G. Ramírez, F. J. Recio, P. Herrasti, C. Ponce-de-León, and I. Sirés, "Effect of RVC porosity on the performance of PbO2 composite coatings with titanate nanotubes for the electrochemical oxidation of azo dyes," Electrochimica Acta, vol. 204, pp. 9-17, 2016/06/20/, 2016.