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TiO_2-Activated Carbon *Elaeis guineensis Jacq* Composite Degraded COD and BOD at Batua Raya Waterways

Firnanelty Rasyid*, Sitti Chadijah, Windasari Windasari

Department of Chemistry, Faculty of Science and Technology, Universitas Islam Negeri Alauddin Makassar, Jl. Sultan Alauddin No.63, Romangpolong, Kec. Somba Opu, Kabupaten Gowa, Sulawesi Selatan 92113
*Corresponding author: firnanelty.rasyid@uin-alauddin.ac.id

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Abstract: Activated carbon is an important material for purification, adsorbent and catalyst in the chemical industry. This research has been carried out to determine the photocatalytic activity of the modified catalyst and adsorbent TiO_2-activated carbon for reduce of COD and BOD of canal water. Carbon composite was successfully synthesized with mixture of two materials that have different physical and chemical properties. Modification TiO_2 with porous material was carried out to determine the optimum mass and contact time for reduce COD and BOD in waterways using photocatalysis method. Activated carbon have made from oil palm bunches through the carbonization process. The composite was tested the optimum TiO_2-activated carbon with a ratio of 2:0.4 g which was applied into canal water for 60 minutes. The result showed that COD value was 99.65% and BOD 94.44%. The result of SEM data image showed that activated carbon blocked TiO_2 clotting and spread on activated carbon. So that TiO_2-activated carbon composite can be used to reduce of COD and BOD level in waterways.

Kata kunci: waterways, photocatalysis, activation, TiO_2-activated carbon

Abstrak: *Karbon aktif merupakan bahan penting untuk pemurnian, adsorben dan katalis dalam industri kimia. Penelitian ini dilakukan untuk mengetahui aktivitas fotokatalitik katalis termodifikasi dan adsorben karbon aktif TiO_2 terhadap penurunan COD dan BOD air kanal. Komposit karbon berhasil disintesis dengan campuran dua bahan yang memiliki sifat fisika dan kimia yang berbeda. Modifikasi TiO_2 dengan material berpori dilakukan untuk menentukan massa dan waktu kontak optimum untuk menurunkan COD dan BOD pada saluran air menggunakan metode fotokatalisis. Karbon aktif dibuat dari tandan kelapa sawit melalui proses karbonisasi. Komposit diuji karbon aktif TiO_2 optimum dengan perbandingan 2:0,4 g yang diaplikasikan ke dalam air kanal selama 60 menit. Hasil penelitian menunjukkan nilai COD sebesar 99,65% dan BOD sebesar 94,44%. Hasil citra data SEM menunjukkan bahwa karbon aktif menghambat penggumpalan TiO_2 dan menyebar pada karbon aktif. sehingga komposit karbon aktif TiO_2 dapat digunakan untuk menurunkan COD dan BOD pada perairan.*

Keywords: *air kanal, fotokatalisis, aktivasi, TiO_2-karbon aktif*

INTRODUCTION

Utilization of waterways as a source of water can be used by the community as part of life. In addition, it is also used as flood control and transportation routes. Currently, effect of industrial, household and other activities that produce waste, both solid and liquid waste, has resulted decreased quality and quantity of clean water resources from year to year, especially in waterways at Batua Raya street, Panakkukang sub-district, Makassar city This can cause serious damage to public health. The decline in water quality due to pollution by waste can be identified physically, chemically and biologically. Chemical Oxygen Demand (COD) and Biological Oxygen Demand (BOD) are parameters for estimating the amount of oxygen in waters to degraded inorganic and organic compound. According to South Sulawesi Governor Regulation Number 69 of 2010 concerning quality standards and criteria for environmental damage quality standard 25 mg/L which is included the second water quality category for fresh water. BOD parameter value is around 3 mg/L (South Sulawesi Governor Regulation Number 69 of 2010). One of ways to reduce levels of COD and BOD in polluted waterways used a photocatalytic process (Bukhari *et al*. 2019). BOD and COD reduction achieved was 95% and 91% respectively with photocatalytic treatment (Bahadur & Bhargava 2019).

A modified photocatalyst as an alternative process for treating polluted waterways can make organic pollutants easily degraded. These results showed that the prepared magnetic photocatalysts have excellent photocatalytic activity and can be easily recovered and reused, which implies the reduction of costs and increases the potential for scale up application (Pereira *et al*. 2019). The process that occurs in photocatalysis cannot be separated from the use of semiconductor materials. Semiconductors are materials that have differences in electrical conductivity between insulators and conductors (Tahya *et al*. 2019). One of the semiconductor materials is titanium dioxide (TiO_2). TiO_2 is the semiconductor material that most often used in the photocatalyst process. The physical and chemical properties of TiO_2 can be seen from its particle size, morphology and crystal phase (Rivera-Utrilla *et al*. 2012). Based on the types of crystal phase, TiO_2 consist of three forms, are anatas, rutile and brukite (Tahya *et al*. 2019). Anatas and bauxite phases are metastable phases which is converted into the rutile phase by heating. TiO_2 as a photocatalyst materials has excellent phytochemical stability, non-toxic and photocatalytic activity (Nasikhudin *et al*. 2018). However, TiO_2 has a high photocatalytic reactivity, so needs material has high adsorption capability for absorption the target compound such as activated carbon (Guo *et al*. 2014). Activated carbon has a porous solid, contains 85-95% carbon and can be used as an absorbent (Singh *et al*. 2016).

Natural material such as oil palm empty bunches (*Elaeis guineensis* Jacq) was potentially useful as material absorbent (Onoja *et al*. 2018). Oil palm empty bunches are solid by produced of the palm oil processing industry. Oil palm empty bunches contained 30-40% cellulose (Dewanti 2018). It potential can be used as activated carbon. Activated carbon (AC) is well known as one efficient support, due to its stability, mechanical resistance, high surface area and optimum porosity (Budianto *et al*. 2019). The absorption of the charcoal is determined by the surface area of the particles. The absorption ability will be higher if the carbon is activated using suitable chemicals or high temperature. The physical and chemical properties will change to be maximum ability (Nasikhudin *et al*. 2018).

TiO_2-activated carbon from oil palm empty bunches composite is a mixture of two different materials that have each physical and chemical properties (Allwar *et al*. 2021). The use of empty palm oil bunches as active carbon is very appropriate in the process of utilizing and processing waste. This composite is also made to cover the weaknesses of TiO_2 which is semiconductor because when it is used as a photocatalyst process it has a weak adsorption power while the photocatalytic process occurs in the adsorbed phase so that the photocatalytic process using the adsorption method. In addition, in the form of powder used in waste degradation, it is difficult to separate, so an alternative to TiO_2 is made by making it a composite. Composites are heterogeneous materials consisting of a matrix and reinforcement (Peñas-garzón *et al*. 2019). Utilized TiO_2-activated carbon catalyst to degradation of the reactive red (Eshaghi & Moradi 2018). One way to determine the quality of TiO_2-activated carbon composites is to use COD and BOD parameters to degrade organic and inorganic polluted canal wastewater.

MATERIALS AND METHODS

Materials

Water from Batua Raya waterways Makassar city, alkaline iodide azide (NaOH-KI), hydrochloric acid (HCl) 1 M, oxalic acid ($H_2C_2O_4$) 0.01 N, sulfuric acid (H_2SO_4) 4 N, sulfuric acid (H_2SO_4) 6 N, starch ($C_6H_{10}O_5$), potassium permanganate ($KMnO_4$) 0.01 N, sodium thiosulfate ($Na_2S_2O_3$), titanium dioxide (TiO_2), oil palm empty bunches (*Elaeis guineensis* Jacq.)

Methods

Preparation of Activated carbon from Oil Palm Empty Bunches

Samples of oil palm bunches are taken from the oil palm fruit that has been harvested. Then do the separation of the oil seeds from the bunches. Then dried under the sun for 6 days.

The dried sample was carbonized into klin drum. Then, sample was sieved with 100 mesh. After that, the sample was heated in an oven at 105 ° C for 10 minutes. The sample was activated with hydrochloric acid (HCl) 1 M for 24 hours. The activated carbon was neutralized with distilled water (H_2O) until pH 7. Samples that have been neutral are then re-oven for drying (Kurnia *et al*. 2014).

Characterization of Activated Carbon

Water Content Test

The empty plates were heated for 30 minutes at 105 °C for 15 minutes (W_0). Furthermore, 1 gram of sample is put into a plate that has known its weight (W_1) then heated into oven for 3 hours at 105 °C. After that for 15-30 minutes into desiccator. Then the plates and the contents were weighed and then heated again for 1 hour (W_2) (AOAC, 82: 1995).

Ash Content Test

The plate that already contains the sample which has determined the water content is placed in the furnace, then slowly heated starting from a temperature of 600 °C for 6 hours. Furthermore, it is cooled in a desiccator until the weight constant (SNI 06-3730-1995).

Making TiO_2-Activated Carbon Photocatalysis

TiO_2 is activated by heating at 200 °C for 4 hours. Then TiO_2 which has been heated, mixed with activated carbon with a variation ratio of TiO_2/activated carbon (w/w) 2:0; 2:0.2; 2:0.4; 2:0.6 and 2:1 (Sudirman, 2015: 349).

Preparation of Water from Waterways

The water from waterways Batua Raya street, Panakkukang sub-district, Makassar city, was taken using Winkler method for BOD testing, the bottle was dipped carefully into the water. The bottle is filled up to 300 mL. Turbulence and air bubbles were avoided during filling in the bottle. Then the sample was analyzed (SNI 6989-59-2008). Determined the temperature and pH (Swashta, 2010: 26).

Photodegradation of canal water using TiO_2-Activated Carbon Composites

Photodegradation was carried out using a UV lamp. TiO_2-activated carbon with certain comparison mixed with 100 mL water from waterways for COD test and 50 mL for BOD test (Aji *et al*. 2016). Next step, each mixture has been stirred with an irradiation time of 60, 120 and 180 minutes (Nadia *et al*. 2017). Then, the results obtained were tested for the reduction in COD and BOD levels. Furthermore, the optimum concentration and contact time obtained were tested by SEM.

Chemical Oxygen Demand (COD) Analysis

100 mL sample into Erlenmeyer which have added boiling stones. Furthermore, a few drops of $KMnO_4$ 0.05 N were added to the sample until occurred pink color. After that, added 5 mL sulfuric acid 4N free of organic substances. Heated at 105 °C. Then 10 mL of $KMnO_4$ 0,05 N standard solution then heated to boiling for 10 minutes. 10 mL of standard oxalic acid solution 0,05 N, then titrated with potassium permanganate 0,05 N until showed pink color and then recorded the volume of of $KMnO_4$ used. (SNI 6989-59-2008).

Biological Oxygen Demand (BOD) analysis

Samples have been prepared in two Winkler bottles are marked with DO_0 and DO_5 notations. DO_5 bottles are stored in an incubator at 20°C for 5 days. Then the DO_0 bottle, added 1 mL of $MnSO_4$ and 1 mL of alkaline iodide azide with the tip of the pipette just above the solution surface. Then it is closed and homogenized until it forms perfect lumps. After 5 minutes to 10 minutes was added 1 mL H_2SO_4 concentrated. Then 50 mL solution were added TiO_2/Activated carbon composite with each comparison. Then stirred with a shaker and exposed to a UV lamp for 60, 120 and 180 minutes. Finally, it is filtered then the filtrate is titrated with $Na_2S_2O_3$ and the starch indicator is added until the blue color disappears. Repeating the work for DO_5 bottles after incubation (SNI 6989-59-2008).

RESULTS AND DISCUSSIONS

Quality of Activated Carbon from Oil Palm Bunches showed on Table 1. The water content test was carried out to determine the remaining water content after the activation process. Based on the results obtained, the water content using the activator obtained 6.9%. Meanwhile, the ash content test was conducted to determine the amount of oxidation in activated carbon. Based on the results obtained in accordance with the Indonesian National Standard (SNI) 06-3730-1995, the ash content is 0.96%.

Characterization of TiO_2-Activated Carbon Composites by Scanning Electron Microscopy (SEM)

The results of the TiO_2-activated carbon morphology through Scanning Electron Microscopy (SEM) showed in Figure 1.

Based on Figure 1a showed the optimum morphological form of TiO_2-activated carbon composites with ratio 2:0.4 for degradation of COD. Figures 1b and 1c showed that results of SEM data of TiO_2-activated carbon optimum for BOD. The results of the TiO_2-activated carbon surface obtained TiO_2 was mixed with activated carbon, which indicates the interaction of elements Ti, O and C on the surface of material (Martins *et al*. 2017). It showed that TiO_2 and activated carbon have completely formed to increase pollutant.

The clumps of TiO_2 particles will spread and stick to the carbon surface, so that the activated carbon is used as a material that has high adsorption ability, inhibited of coagulation between TiO_2. It caused the TiO_2 surface have big areas and increase the photocatalytic activity of TiO_2 (Septiani *et al*. 2015: 4) so the absorption that occurs will be more optimal.

Photodegradation of Water from waterways with TiO_2-Activated Carbon Composite

Based on Table 2, the water analysis in the Batua Raya waterways contained pollutants. This condition indicated that BOD and COD values obtained through the quality standards based on Government Regulation No. 82 of 2001. This indicates that the more organisms present in the waters, the growth of algae and other plants increases indicating a high level of pollution. The condition can be reduced by the photocatalytic method (Fernandes *et al*. 2020).

Table 1. Quality of activated carbon for oil palm empty bunches

Parameter	Carbon Powder (%)	Standard
Water content	6,90	15
Ash content	0,96	10

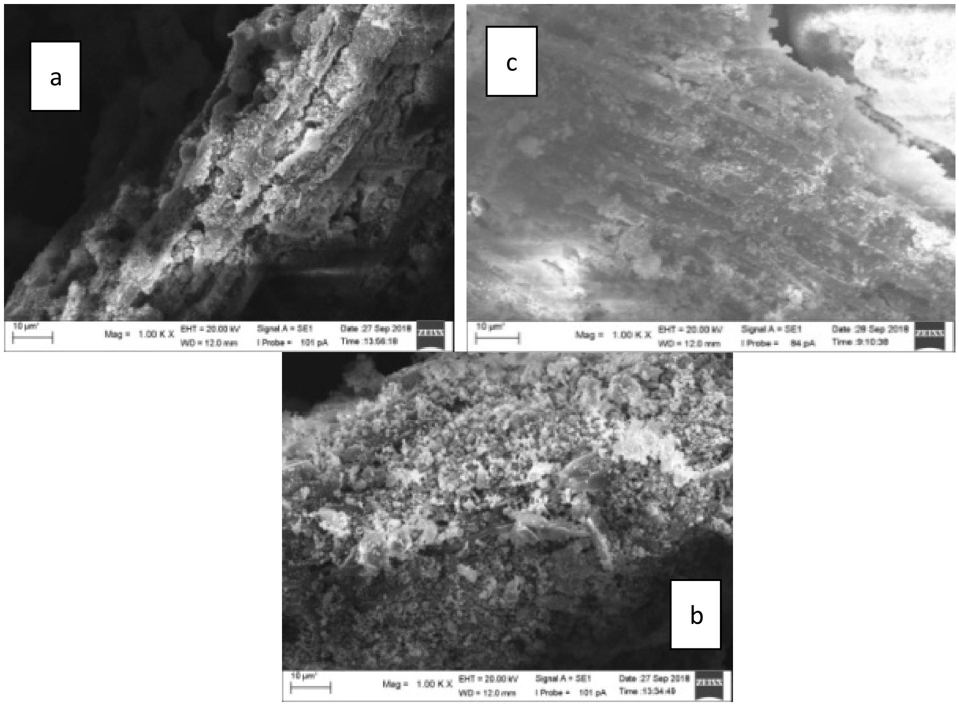

Figure 1. Morphology of TiO_2-activated carbon

Table 2. Result of BOD and COD content in waterways

Parameters	Unit	Result test	Standard of Waterways
BOD	mg/L	7.20	3
COD	mg/L	43.45	25
pH	-	5.31	6.0-9.0
Temperature	ºC	29	± 3 °C

Table 3. Result of degradation of COD with TiO_2-activated carbon

Mass of TiO_2-activated carbon	COD					
	60 minutes	Efficiency (%)	120 minutes	Efficiency (%)	180 minutes	Efficiency (%)
2:0	34.76	20.00	31.60	27.27	33.18	23.63
2:0.2	28.44	34.54	7.90	81.81	23.70	45.45
2:0.4	0.15	99.65	18.96	56.36	15.80	63.63
2:0.6	17.38	60.00	9.48	78.18	22.12	49.09
2:1	35.55	18.18	39.50	9.09	34.76	20.00

Table 3 showed results of photodegradation of waterways using TiO_2-activated carbon with COD. Based on Table 2, it can be seen that the optimum concentration and contact time occurs with ratio of TiO_2-activated carbon 2:0.4 with a long stirring and irradiation for 60 minutes. Result of degradation of COD obtained 99.65% which has better absorption. Its mean TiO_2-activated carbon have successfully as an absorbent. For BOD (Table 4), activated carbon was added 0.4 grams, BOD value decrease until 94.44%. Increasing of amount of activated carbon mixed with TiO_2 in the water would was caused the interaction be imperfect because the amount of TiO_2-activated carbon unstable fot degrade organic and inorganic compounds in the waterways. The ability of TiO_2-activated carbon composites was successfully as photocatalysts materials.

Photocatalytic TiO_2-activated carbon produces hydroxyl radicals which are not only obtained from photolysis of water but also obtained from the results

Table 4. Result of degradation of BOD with TiO_2-activated carbon

Mass of TiO_2-activated carbon	BOD					
	60 minutes	Efficiency (%)	120 minutes	Efficiency (%)	180 minutes	Efficiency (%)
2:0	0.8	88.88	0.8	88.88	0.8	88.88
2:0.2	1.2	83.33	2.8	61.11	2.4	66.66
2:0.4	0.4	94.44	1.6	77.77	1.2	83.33
2:0.6	1.6	77.77	2.4	66.66	3.6	50.00
2:1	4.0	44.44	3.2	55.55	4.8	33.33

of the interaction between water and the resulting holes in the valence band according to the reaction equation (1). So that the presence of hydroxyl radicals in the reaction system will increase in the presence of TiO_2-activated carbon photocatalysts. The hydroxyl radicals formed in accordance with equations (2), (3) and (4) on the photocatalytic surface are generated after photocatalyst absorbs light with the appropriate energy, so there is a transfer of electrons from the valence band to the conduction band leaving holes in the valence band. Equation 5 then shows that the air flowing into the system can prevent recombination between electrons in the conduction band and holes in the valence band. The hydroxyl radicals produced together with oxygen then oxidize organic compounds according to equation 6. Hydroxyl radicals are very reactive species that attack organic molecules so that they degrade which then produce simpler compounds such as CO_2 and H_2O (Yuningrat *et al*. 2015).

CONCLUSION

TiO_2-activated carbon composite was successfully synthesized from TiO_2 and oil palm bunches. The highest efficiency of the catalyst in the degradation of COD and BOD levels in waterways with ratio 2:0.4 (b/b) for 60 minutes contact time gave 99.65% and 94.44% degradation. Result of SEM analysis showed activated carbon can be inhibited the clumping of TiO_2 particles so spread on the surface of carbon caused absorption that occurs more optimal.

REFERENCES

Aji, N.R., Wibowo, E.A.P., Ujiningtyas, R., Wirasti, H. & Widiarti, N. (2016). Sintesis komposit TiO_2-bentonit dan aplikasinya untuk penurunan BOD dan COD Air Embung UNNES. *Jurnal Kimia Valensi*. **2(2)**: 114-119.

Allwar, A., Fatima, M.N. & Wiyantoko, B. (2021). Synthesis and characterization of TiO_2 nanoparticles doping on cellulose as adsorbent for removal of rhodamine B in aqueous solution. *EKSAKTA: Journal of Sciences and Data Analysis*. **2(1)**: 45-54.

Budianto, A., Kusdarini, E., Effendi, S.S.W. & Aziz, M. (2019). The production of activated carbon from Indonesian mangrove charcoal. In *IOP Conference Series: Materials Science and Engineering*. **462(1)**: 012006.

Bahadur, N. & Bhargava, N. (2019). Novel pilot scale photocatalytic treatment of textile & dyeing industry wastewater to achieve process water quality and enabling zero liquid discharge. *Journal of Water Process Engineering*. **32**: 100934.

Bukhari, K., Ahmad, N., Sheikh, I. A. & Akram, T. M. (2019). Effects of different parameters on photocatalytic oxidation of slaughterhouse wastewater using TiO. *Polish Journal of Environmental Studies*. **28(3)**: 1-10.

Dewanti, D.P. (2018). Cellulose Potential of Empty Fruit Bunches Waste as The Raw Material of Bioplastics Environmentally Friendly. *Jurnal Teknologi Lingkungan*. **19(1)**: 81–88.

Eshaghi, A. & Moradi, H. (2018). Optical and photocatalytic properties of the Fe-doped TiO_2 nanoparticles loaded on the activated carbon. *Advanced Powder Technology*. **29(8)**: 1879-1885.

Fernandes, A., Makoś, P., Wang, Z. & Boczkaj, G. (2020). Synergistic effect of TiO_2 photocatalytic advanced oxidation processes in the treatment of refinery effluents. *Chemical Engineering Journal*. **391**: 123488.

Guo, X., Dai, J., Zhang, K., Wang, X., Cui, Z. & Xiang, J. (2014). Fabrication of N-doped TiO_2/activated carbon fiber composites with enhanced photocatalytic activity. *Textile Research Journal*. **84(17)**: 1891-1900.

Kurnia, S., Wahyuni, N. & Zaharah, T.A. (2014). Sintesis dan interkalasi pigmen norbixin pada bentonit terpilar TiO_2. *Jurnal Kimia Dan Kemasan*. **3(4)**: 2–6.

Martins, A.C., Cazetta, A. L., Pezoti, O., Souza, J. R. B., Zhang, T., Pilau, E.J., Asefa, T. & Almeida, V.C. (2017). Sol-gel synthesis of new TiO_2/activated carbon photocatalyst and its application for degradation of tetracycline. *Ceramics International*. **43(5)**: 4411–4418.

Nadia, A., Fauziah, A., Mayori, E. & Sunardi. (2017). Potential of lignocellulosic oil palm waste in south kalimantan for bioethanol and xylitol production. *Jurnal Inovasi Pendidikan Sains*. **8(2)**: 41–51.

Nasikhudin, Diantoro, M., Kusumaatmaja, A. & Triyana, K. (2018). Study on photocatalytic properties of TiO_2 nanoparticle in various pH condition. *Journal of Physics: Conference Series*. **1011(2018)**: 012069.

Onoja, E., Chandren, S., Abdul Razak, F. I., Mahat, N. A. & Wahab, R. A. (2019). Oil palm (*Elaeis guineensis*) biomass in Malaysia: the present and future prospects. *Waste and Biomass Valorization*. **10**: 2099-2117.

Peñas-Garzón, M., Gómez-Avilés, A., Bedia, J., Rodriguez, J. J. & Belver, C. (2019). Effect of activating agent on the properties of TiO_2/activated carbon heterostructures for solar photocatalytic degradation of acetaminophen. *Materials*. **12(3)**: 378.

Pereira, d.O.L., Sales, I. M., Zampiere, L. P., Vieira, S. S., do Rosário Guimarães, I. & Magalhães, F. (2019). Preparation of magnetic photocatalysts from TiO_2, activated carbon and iron nitrate for environmental remediation. *Journal of Photochemistry and Photobiology A: Chemistry*. **382**: 111907.

Rivera-Utrilla, J., Sánchez-Polo, M. & Ocampo-Pérez, R. (2012). Role of activated carbon in the photocatalytic degradation of 2, 4-dichlorophenoxyacetic acid by the UV/TiO2/activated carbon system. *Applied Catalysis B: Environmental*. **126**: 100-107.

Singh, P., Vishnu, M.C., Kumar, K., Borthakur, A., Srivastava, P., Pal, D.B., Tiwary, D. & Kumar, P. (2016). Journal of water process engineering photocatalytic degradation of acid red dye stuff in the presence of activated carbon-TiO_2 composite and its kinetic enumeration. *Journal of Water Process Engineering.* **12**: 20–31.

Tahya, C.Y., Irawati, W., Karnelasatri, K. & Purba, F. J. (2019). Synthesis and characterization of TiO_2-CaO and TiO_2-CaO-Fe_2O_3 photocatalyst for removal of catechol. *Molekul*. **14(2)**: 140-148.

Yuningrat, N.W., Oviantari, M.V. & Gunamantha, I. M. (2015). Fotodegradasi senyawa organik dalam lindi dengan menggunakan katalis TiO_2 terimobilisasi pada plat kaca. *Sains Dan Teknologi*. **4(2)**: 642–654.