Vol 01 2022, pp 1-10
e-ISSN: XXXX-XXXX
DOI: https://doi.org/10.54482/ELECTROLYTE/

PROTOTYPE OF HEXAGONAL PHOTO-REACTOR FOR DEGRADATION HUMIC ACID USING CU-ZNO AS A CATALYST IN VISIBLE LIGHTS

Hana Safitri[a], Fauzan Yan Hawari[b], Ghoury Kharisma Anjali[c], Intan Anika Putri[d], Sintia Noveliza[e], Rela Faradina[f]

[a]Magister Programme of Biochemistry, Postgradute, Central Luzon State University, Nueva Ecija, Philippines
[b,c,d,e]Department of Chemistry, Faculty oh Mathematics and Natural Science, Universitas Negeri Padang, Jl. Prof. Dr. Hamka, Air Tawar Barat, Padang Utara, West Sumatera, Indonesia, 25171
[f]Magister Programme of Educational Chemistry, Postgraduate, Universitas Negeri Padang, Jl. Prof. Dr. Hamka, Air Tawar Barat, Padang Utara, West Sumatera, Indonesia, 25171

*Coresponding email: fauzanyanhawari99@gmail.com

ABSTRACT

Humic acid is a heterogeneous organic compound that is carcinogenic in peat water and is very difficult to degrade biologically. Water is a source of life, therefore the need for clean water is increasing. This study aims to carry out the degradation of humic acid using the photocatalytic method. Photocatalysis is the degradation of humic acid using light in the presence of a photocatalyst in the reaction process. The photocatalyst used in this study was 7% Cu doped ZnO. The Cu doped ZnO used with a band gap of 2.57 eV and a particle size of 27 nm. In this study, the humic acid degradation process used a hexagonal photo reactor with various stirring speeds of 500, 1000, 1500 rpm and without stirring. The degradation process is carried out using outdoor light (direct sun). The light intensity can be measured using lightmeters on the front and rear of the reactor. The degradation process uses variations in irradiation time of 1, 2, 3, 4 and 5 hours. The degradation results were measured using a UV-Vis spectrophotometer to see the absorbance before and before degradation. The results of this study obtained the highest percentage degradation at the speed of each stirring of 500 rpm of 90.09% at 5 hours of irradiation, 1000 rpm of 97.37% at 5 hours of irradiation, 1500 rpm of 97.79% at 5 hours of irradiation. hours and without stirring of 71.71% at 5 hours of irradiation. The maximum degradation concentration in this study was obtained at a stirring speed of 1500 rpm and an irradiation time of 5 hours. The speed and irradiation time have an influence on the degradation results obtained.

Keywords: Humic Acid, Photocatalysis, Cu Doping Zno, Degradation Concentration

1. INTRODUCTION

Peat water is surface water that is found in peat areas.[1][2] The properties of peat water have a high acidity, color intensity brownish red, ion particles and high organic compound.[3][4] One of them is humic acid (HA). Humic acid (HA) is a heterogeneous organic compound with high molecular weight which is difficult to degraded biologically.[5][6] If HA is found in drinking water, it can interfere with water quality and health. Characteristic of drinking water is contamined the color is brownish red and low pH.[29] HA is precursor of disenfection by products (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAAs), which are mutagenic end carsinogenic. Many experiements method to removal HA in drinking water, such as filtration, coagulation, electrocoagulation, adsorption, photocatalysis and others.[30]

Photocatalysis a efficient method to elimination HA in water.[7] Photocatalysis is reaction photolysis using catalyst in the process.[9] Catalyst will be active when exposed light.[10][11]

Catalyst used degradation HA is ZnO, because it cheap, low cost and synthesis process is easy.[12][13] Addition, ZnO has characteristic of band gap 3.37 eV, high production ·OH.[14][15] High band gap energy of ZnO make ther are not applied in visible light.[16] Therefore, it is necessary to modify ZnO so that it can be applied to visible light. Modification is done by doped with metal ions. The metals ion that is suitable for use is Cu, because it is known to reduce the ZnO band gap energy.[27][28] Low band gap from ZnO can make it applied in visible light.[22][23]

2. LITERATURE REVIEW

ZnO doped Cu with nano particles size make its activity better. Small particles sizes increases surface area and many active cite. The produce ZnO doped Cu in nano particles with sol-gel method.

Photodegradation of HA using visible light is starting to develop using a modified catalyst.[17] This study goals to degrade HA using nano ZnO doped Cu in visible light for paet water treatment.[26]

To the best of our knowledge the visible light photocatalysis of microplastics particles and in water flow system in order to mimic the real situation as in water treatment facilities and wastewater treatment plants has not been reported.[8] Therefore, this work investigates the photocatalytic degradation of microplastics spherical particles suspended in water by visible light irradiation of ZnO NRs immobilized onto glass fibers substrates (photocatalyst) in a flow through system.[18][19] PP microplastics with an average particle size of 154.8 ± 1.4 μm was selected as pollutant model because it is a major aquatic pollutant due to its lower density than water.[20][21] Thus PP has the potential of being mistaken as a feed even by smaller aquatic animals and fishes which search for food on surface of water complicated by the fact that the half-life of PP is a few hundred years. Furthermore, the photocatalytic activity of ZnO NRs is evaluated by considering the evolution of the carbonyl index parameter and the main water soluble by-products formed during the degradation process was identified using GC-MS.[24][25]

3. EXPERIMENTAL

Material and Methods

The tools and materials used in this study are beaker, measuring cup, volumetric flask 1 L, analytical balance, stirring rod, hexagonal cell phone reactor, drop pipette, humic acid, aquades, $Zn(CH_3COO)_2.H_2O$, $Cu(CH_3COO)_2.H_2O$, isopropanol, MEA (monoetanolamin), XRD, UV-Vis Spectrophotometer, DRS UV-Vis Spectra.

General procedure

Synthesis of Nano ZnO doped Cu with sol gel method

2.743 grams of $Zn(CH_3COO)_2.H_2O$ dissolved with 50 ml of isopropanol in 100 mL beaker glass and covered with aluminium foil. Stir it a magnetic for 40 minutes. Added 0,68 grams $Cu(CH_3COO)_2.H_2O$ as doping material to doping 7%, again covered with aluminium foil and strirred using a magnetic stirrer for 40 minutes. After that, Added MEA (monoetanolamin) 1.4 mL and stirring was continued for 90 minutes resulting in soles. The soles were left for one night, after which they were put into a vaporizer cup, dried in an oven at 110 ^{0}C for 1 hour. The gel formed is put into the furnace, heated at temperature of 500 ^{0}C for 2 hours. The formed product is stored in the desicator, and crushed. After that it was tested with XRD and DRS UV-Vis Spectra.

Design Reactor

The design of the reactor begins with providing a transparent glass with a thickness of 3 mm and then cutting the glass with a height of 15 cm and a width of 7 cm then the glass is glued to form a hexagon. The glass that has been formed is then in the upper part of the hole as the entry point of the stirrer, the stirrer is connected to the dynamo so that the stirrer can rotate in figure 1.

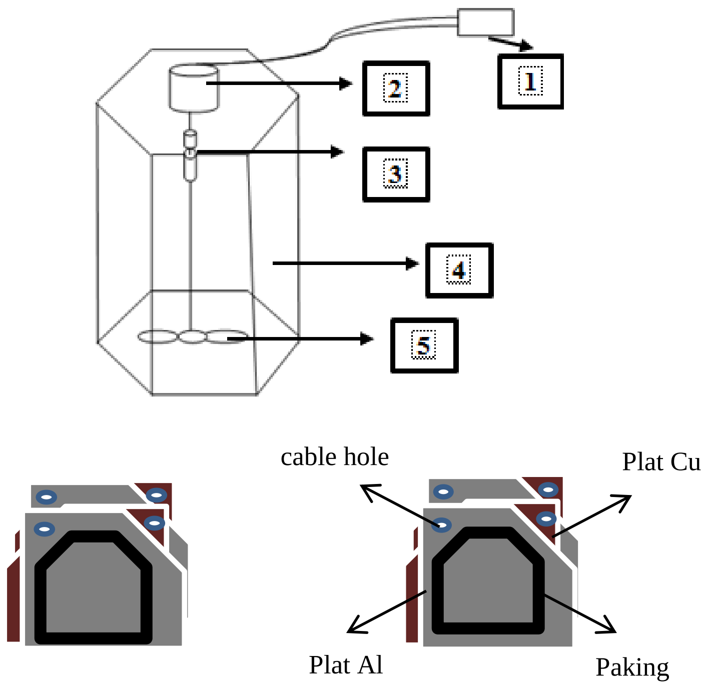

Figure 1. Design reactor

Information :

1. *Voltmeter*
2. *Dynamo*
3. *The connection between the dynamo and the stirrer*
4. *Transparent glass*
5. *Propellers*

Degradation HA using ZnO doped Cu 7%

Preparation samples by weighing 0.02 grams of HA and then dissolving it in 1000 mL of distilled water. Then measure the absorbance using a UV-Vis spectrophotometer. Added 0.06 grams of 7% Cu-doped ZnO catalyst into the mobile hexagonal reactor, then added 200 mL of 20 ppm HA solution, carried out the degradation process using variations in irradiation time of 1, 2, 3, 4 and 5 hours and stirring speed of 500, 1000, 1500 rpm and without stirring, then measure the absorbance of HA using a UV-Vis spectrophotometer.

4. RESULTS AND DISCUSSION

Synthesis of Nano ZnO doped Cu with sol gel method

Nano ZnO doped Cu was synthesized with a doped 7% to producing a bluish-gray color, the presence of a blue color indicated the presence of Cu contained in ZnO. Nano ZnO doped Cu. Nano ZnO doped Cu has a yielding and soft texture can be seen in figure 2.

Figure 1. ZnO doped Cu 7%

Nano ZnO doped Cu was tested using XRD and UV-Vis DRS Spectrophotometer. XRD test results show the nano size of 7% ZnO doped Cu is 27 nm. A nanomaterial is a material with a size in the range from 1-100 nm. catalysts in nano size will improve performance due to the increase in surface area and active sites. Measurements using a DRS UV-Vis spectrophotometer showed the results of a band gap catalyst. band gap of 7% Cu doped ZnO catalyst is 2.57 eV.

Design Reactor

The reactor is where the photocatalysis process takes place. In this study, the photocatalytic reactor used was a mobile hexagonal reactor. In this reactor, light enters from all directions, but measurements for light intensity are carried out from the front and back of the reactor.

Degradation HA using ZnO doped Cu 7%

Testing HA 20 ppm using a UV-Vis spectrophotometer to see the maximum wavelength and initial absorbance of the HA solution, the maximum wavelength was obtained at 269 nm can be seen in figure 3.

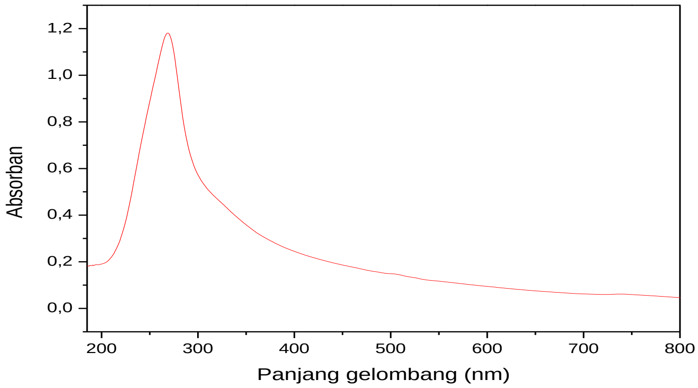

Figure 2. Maximum wavelength HA

This research was conducted using a hexagonal Degration mobile reactor with several variations of treatment to get maximum results. Variations carried out were stirring speeds of 500, 1000, 1500 and without stirring with variations in irradiation time of 1, 2, 3, 4 and 5 hours. The result degradation showed a decrease in concentration of HA, according to the following figure 4.

Table 1. Degradation of HA without stirring using ZnO doped Cu 7%

Time (Hours)	*ABS*	*% D*	*Front luks (LX)*	*Rear luks (LX)*
1	0.369	68.75	10842.11	6494.33
2	0.365	69.09	11044.25	8.950.50
3	0.345	70.78	17385.11	12750.13
4	0.340	71.21	14597.62	11925.16
5	0.334	71.71	18080.03	15681.13

Table 2. Degration of HA at 500 rpm using ZnO doped Cu 7%

Time (Hours)	*ABS*	*% D*	*Front luks (LX)*	*Rear luks (LX)*
1	0.151	87.21	11174.06	8908.71
2	0.123	89.58	14533.08	11047.25
3	0.128	89.16	11409.16	8897.16
4	0.123	89.58	15293.70	12893.91
5	0.117	90.09	17625.83	12985.87

Table 3. Degration of HA at 1000 rpm using ZnO doped Cu **7%**

Time (Hours)	*ABS*	*% D*	*Front luks (LX)*	*Rear luks (LX)*
1	0.086	92.71	13236.66	9471
2	0.032	97.29	15910.25	12017.91
3	0.040	96.61	13539.16	10408.88
4	0.031	97.37	21088	14979.16
5	0.031	97.37	18166.26	15358.76

Table 4. Degradation of HA at 1500 rpm using ZnO doped Cu 7%

Time (Hours)	*ABS*	*% D*	*Front luks (LX)*	*Rear luks (LX)*
1	0.054	95.42	14751	11632.33
2	0.047	96.02	18177.33	14223.16
3	0.033	97.02	17304.22	13675.50
4	0.040	96.61	15664.75	12360.70
5	0.026	97.79	20125.33	16949.66

1) Degradation of HA without stirring

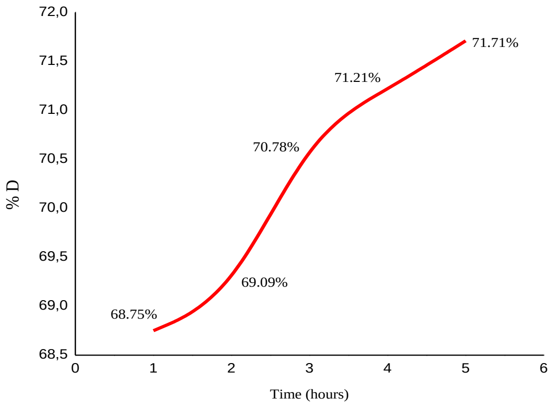

Figure 4. Degradation of HA without Stirring

2) Degration of HA at speed 500 rpm

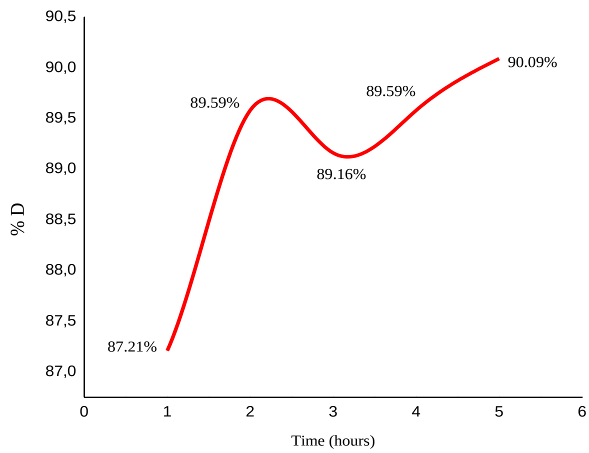

Figure 5. Degradation of HA at Speed 500 rpm

3) Degration of HA at speed 1000 rpm

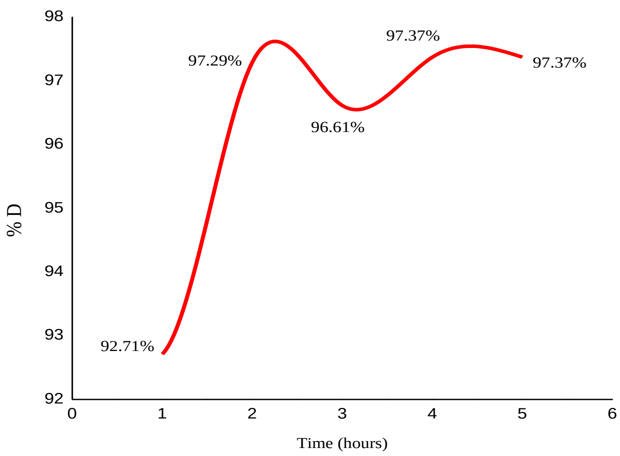

Figure 6. Degradation of HA at Speed 1000 rpm

4) Degration of HA at speed 1500 rpm

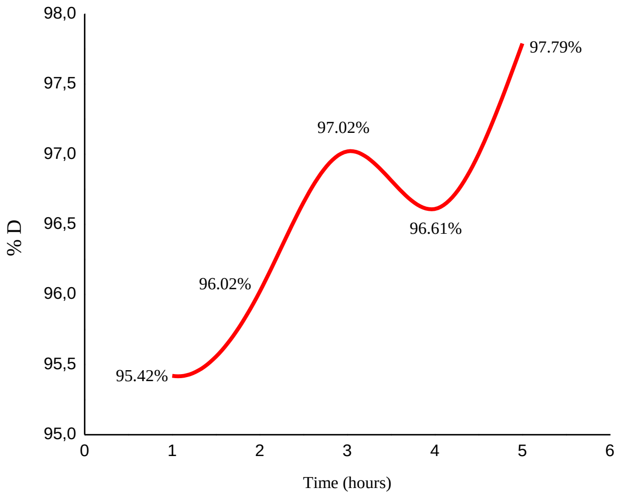

Figure 7. The degradation graph HA using ZnO doped Cu

The significant difference in results using agitation indicates that there is an effect of stirring on the performance of the catalyst. The concentration of degradation obtained is linear with the length of irradiation time [18]. The longer the irradiation time, the higher the results. This is because the formation of hydroxide radicals in the reaction process increases with the longer irradiation. Photodegradation using a 7% Cu-doped ZnO photocatalyst occurs due to the excitation of electrons from the conduction band to the valence band of a catalyst. This excitation will produce a highly reactive hydroxyl radical that is useful in the degradation process. When there is excitation of electrons from the valence band to the conduction band, the excited electrons will react with oxygen to form superoxide anions. While one electron in the valence band will bind directly to water molecules which will produce hydroxyl radicals (•OH) which are useful in the degradation process and produce H^+. Then this superoxide anion will bind to the H^+ in the solution to produce hydrogen peroxide which is also useful for the formation of hydroxide radicals. In addition, in photodegradation using this photocatalyst, photolysis reactions also occur in it which will also produce hydroxide radicals. The hydroxide radicals formed are useful for breaking bonds in HA which produce simple molecules such as CO_2 dan H_2O.

5. CONCLUSION

The percentage of degradation is strongly influenced by light intencity, increasing light intencity in the process will make the degradation increase. The speed of stirring wil also affect the degradation result, with the safter stirring the percentage of degradation also increase.

REFERENCES

[1] Qadafi, M., Notodarmojo, S., & Zevi, Y. (2021). Performance of microbubble ozonation on treated tropical peat water: Effects on THM4 and HAA5 precursor formation based on DOM hydrophobicity fractions. *Chemosphere*, *279*, 130642.

[2] Zainul, R. (2016). Determination of the half-life and the quantum yield of ZnO semiconductor photocatalyst in humic acid. *Der Pharmacia Lettre*, *15*(8), 176-179.

[3] Yulianto, F. E., Mochtar, N. E., & Amin, M. M. R. (2022). PHYSICAL AND ENGINEERING PROPERTIES OF PEAT SOIL STABILIZED WITH THE ADMIXTURE OF CACO3+ RICE HUSK ASH DUE TO WATER INFILTRATION FROM SURROUNDING AREAS. *Journal of Applied Engineering Science*, 1-9.

[4] Rahmadhanty, S., & Zainul, R. (2018). Design Of Humat Acid Solid Solution Reactor Through Phototransformation Of Copper Oxide (Cuo) Semiconductor Plate.

[5] Ali, M., Awan, F. U. R., Ali, M., Al-Yaseri, A., Arif, M., Sánchez-Román, M., ... & Iglauer, S. (2021). Effect of humic acid on CO2-wettability in sandstone formation. *Journal of Colloid and Interface Science*, *588*, 315-325.

[6] Djasli, Y. A., Purnamasari, D., & Zainul, R. (2020, March). Study of dynamically catalytic system on humic acid phototranformator. In *Journal of Physics: Conference Series* (Vol. 1481, No. 1, p. 012037). IOP Publishing.

[7] Zhang, Y. H., Liu, M. M., Chen, J. L., Fang, S. M., & Zhou, P. P. (2021). Recent advances in Cu 2 O-based composites for photocatalysis: a review. *Dalton Transactions*, *50*(12), 4091-4111.

[8] He, X., Wu, M., Ao, Z., Lai, B., Zhou, Y., An, T., & Wang, S. (2021). Metal–organic frameworks derived C/TiO2 for visible light photocatalysis: Simple synthesis and contribution of carbon species. *Journal of Hazardous Materials*, *403*, 124048.

[9] Shi, Q., Tao, Y., Krechmer, J. E., Heald, C. L., Murphy, J. G., Kroll, J. H., & Ye, Q. (2021). Laboratory Investigation of Renoxification from the Photolysis of Inorganic Particulate Nitrate. *Environmental science & technology*, *55*(2), 854-861.

[10] Palos, R., Kekäläinen, T., Duodu, F., Gutiérrez, A., Arandes, J. M., Jänis, J., & Castaño, P. (2021). Detailed nature of tire pyrolysis oil blended with light cycle oil and its hydroprocessed products using a NiW/HY catalyst. *Waste Management*, *128*, 36-44.

[11] Zainul, R., Dewata, I., & Oktavia, B. (2019, April). Fabrication of hexagonal photoreactor indoor lights. In *Journal of Physics: Conference Series* (Vol. 1185, No. 1, p. 012007). IOP Publishing.

[12] Zainul, R., Effendi, J., & Mashuri, M. (2019). Phototransformation of Linear Alkylbenzene Sulphonate (LAS) Surfactant Using ZnO-CuO Composite Photocatalyst. *KnE Engineering*, 235-247.

[13] Krishnan, S., & Shriwastav, A. (2021). Application of TiO2 nanoparticles sensitized with natural chlorophyll pigments as catalyst for visible light photocatalytic degradation of methylene blue. *Journal of Environmental Chemical Engineering*, *9*(1), 104699.

[14] Singh, Y., Singh, N. K., Sharma, A., Singla, A., Singh, D., & Abd Rahim, E. (2021). Effect of ZnO nanoparticles concentration as additives to the epoxidized Euphorbia Lathyris oil and their tribological characterization. *Fuel*, *285*, 119148.

[15] Sanjaya, H., & Zainul, R. (2016). Synthesis and Electrical Properties of ZnO-ITO and Al-ITO thin Film by Spin Coating Technique Through Sol Gel Process.

[16] Kale, V., Hunge, Y. M., Kamble, S. A., Deshmukh, M., Bhoraskar, S. V., & Mathe, V. L. (2021). Modification of energy level diagram of nano-crystalline ZnO by its composites with ZnWO4 suitable for sunlight assisted photo catalytic activity. *Materials Today Communications*, *26*, 102101.

[17] Chaubey, B., Narwal, P., Khandelwal, A., & Pal, S. (2021). Aqueous photo-degradation of Flupyradifurone (FPD) in presence of a natural Humic Acid (HA): A quantitative solution state NMR analysis. *Journal of Photochemistry and Photobiology A: Chemistry*, *405*, 112986.

[18] Othman, A. R., Hasan, H. A., Muhamad, M. H., Ismail, N. I., & Abdullah, S. R. S. (2021). Microbial degradation of microplastics by enzymatic processes: a review. *Environmental Chemistry Letters*, *19*(4), 3057-3073.

[19] Hidayati, R., & Zainul, R. (2019). Studi Termodinamika Transpor Ionik Natrium Klorida Dalam Air dan Campuran Tertentu.

[20] Du, Y., Xu, X., Liu, Q., Bai, L., Hang, K., & Wang, D. (2022). Identification of organic pollutants with potential ecological and health risks in aquatic environments: Progress and challenges. *Science of The Total Environment*, *806*, 150691.

[21] Li, Y., Wang, M., Chen, X., Cui, S., Hofstra, N., Kroeze, C., ... & Strokal, M. (2022). Multi-pollutant assessment of river pollution from livestock production worldwide. *Water research*, *209*, 117906.

[22] Upadhaya, D., & Purkayastha, D. D. (2022). Self-cleaning activity of CuO/ZnO heterostructure: A synergy of photocatalysis and hydrophilicity. *Journal of the Taiwan Institute of Chemical Engineers*, *132*, 104216.

[23] Zainul, R., Effendi, J., & Mashuri, M. (2019). Phototransformation of Linear Alkylbenzene Sulphonate (LAS) Surfactant Using ZnO-CuO Composite Photocatalyst. *KnE Engineering*, 235-247.

[24] Elumalai, N., Prabhu, S., Selvaraj, M., Silambarasan, A., Navaneethan, M., Harish, S., ... & Ramesh, R. (2022). Enhanced photocatalytic activity of ZnO hexagonal tube/r-GO composite on degradation of organic aqueous pollutant and study of charge transport properties. *Chemosphere*, *291*, 132782.

[25] Zainul, R., Effendi, J., & Mashuri, M. (2019). Phototransformation of Linear Alkylbenzene Sulphonate (LAS) Surfactant Using ZnO-CuO Composite Photocatalyst. *KnE Engineering*, 235-247.

[26] Pirzada, T., Chandio, W. A., Kalhoro, M. A., Ali Talpur, M. M., Mirbahar, W. A., Solangi, A. G., ... & Kerio, R. (2022). Synthesis and Characterization of Humic Acid Hybrid Zinc Oxide Nanoparticles: Applications on Brassica campestris Germination. *Sarhad Journal of Agriculture*, *38*(1).

[27] Ye, Z., Zhao, Y., Zhang, H., Shi, Z., Li, H., Yang, X., ... & Tang, Y. (2022). Mesocrystal morphology regulation by “alkali metals ion switch”: Re-examining zeolite nonclassical crystallization in seed-induced process. *Journal of Colloid and Interface Science*, *608*, 1366-1376.

[28] Zainul, R. (2015). Study of Pb (II) biosorption from aqueous solution using immobilized Spirogyra subsalsa biomass. *Journal of Chemical and Pharmaceutical Research*, *11*(7), 715-722.

[29] Shi, Y., Ren, X., Zheng, H., Zhang, Y., & Zuo, Q. (2022). Hierarchical 13X zeolite/reduced graphene oxide porous material for trace Pb (II) capturing from drinking water. *Microporous and Mesoporous Materials*, *329*, 111540.

[30] Chen, K., Feng, Q., Feng, Y., Ma, D., Wang, D., Liu, Z., ... & Feng, J. (2022). Ultrafast removal of humic acid by amine-modified silica aerogel: Insights from experiments and density functional theory calculation. *Chemical Engineering Journal*, 135171.