Indonesian Journal of Material Research
e-ISSN: 2987-1654
Vol. 2, No. 1, March 2024

Research Paper

Selective Adsorption of Cationic and Anionic Dyes using Ni/Al Layered Double Hydroxide Modified with *Eucheuma cottonii*

Sahrul Wibiyan[1,2], Idha Royani[3], Aldes Lesbani[1,2]*

[1] *Magister Program of Materials Science Graduate School of Universitas Sriwijaya, Palembang, 30139, Indonesia*
[2] *Research Center of Inorganic Materials and Coordination Complexes, Universitas Sriwijaya, Palembang, 30139, Indonesia*
[3] *Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Sriwijaya, Palembang, 30662, Indonesia*
***Corresponding author**: aldeslesbani@pps.unsri.ac.id

Abstract

This study investigates the selective adsorption capabilities of Ni/Al Layered Double Hydroxide (LDH) modified with *Eucheuma cottonii* for the removal of cationic and anionic dyes from aqueous solutions. The primary objective was to evaluate the efficiency and selectivity of these modified adsorbents towards different dyes, including rhodamine-b, malachite green, methylene blue (cationic dyes), and direct yellow, methyl orange, direct green (anionic dyes). The modification process aimed to enhance the adsorption properties of LDHs, leveraging the natural adsorption capabilities of *Eucheuma cottonii*. Experimental results demonstrated significant differences in adsorption percentages among the tested dyes, with malachite green showing the highest adsorption efficiency among cationic dyes, indicating a strong affinity of the modified adsorbents towards cationic dyes. However, the ability to also adsorb anionic dyes suggests the dual-functionality of the modified LDHs, making them versatile agents for dye removal in water treatment applications.

Keywords

Layered Double Hydroxide, *Eucheuma cottonii*, Dye Selectivity

Received: 29 December 2023, Accepted: 8 March 2024
https://doi.org/10.26554/ijmr.20242118

1. INTRODUCTION

Material modification is the process of altering the physical, chemical, or structural properties of a material to enhance its performance, functionality, or applications in various fields. This process may involve adding new components, changing compositions, or modifying the surface of the material. For example, in the context of absorbing pollutants from water, material modification can be performed to enhance the adsorption capacity of the material towards pollutants such as dyes (Bagherzadeh et al., 2024).

Material modification is carried out to enhance the efficiency and adsorption capacity of the material towards specific contaminants in water. This modification may involve changes in the physical structure, addition or alteration of functional groups on the material surface, or combining materials with other components to create composites. The primary goal is to achieve more effective, selective, and efficient contaminant removal from both energy and cost perspectives. Specifically, the objective of modification for dye selectivity is to create materials that not only can adsorb dyes from solutions with high capacity but also can distinguish and select specific dyes from a mixture of dyes or other contaminants. This is crucial in wastewater treatment applications, where mixtures of various dyes and other contaminants are often encountered. By enhancing the material's selectivity towards specific dyes, the wastewater treatment process becomes more efficient, reducing the consumption of chemicals and energy, and improving the quality of the resulting water (Salem et al., 2022).

LDH (Layered Double Hydroxides) have advantages in material modification as selective adsorbents for specific dyes, including the ability to alter the chemical properties and total charge of the brucite-like layers through variations in composition and properties of components. This enables LDH to incorporate organic and inorganic groups with different properties through anion exchange, thus enhancing its selectivity towards specific dyes (Dai et al., 2023). LDH can be modified with organic materials such as graphene oxide (Amri et al., 2023; Amri et al., 2024), magnetic biochar (Zahara et al., 2023), hydrochar from rambutan peels (Normah et al., 2021) and activated carbon (Ahmad et al., 2023a). In addition, LDH can also be modified with inorganic compounds such as zinc oxide (Mohadi et al., 2023), titanium oxide (Ahmad et al., 2022), graphite (Siregar et al., 2021) and polyoxometalate (Hanifah et al., 2023). Organic materials often contain specific functional groups that can selectively interact with certain dyes through hydrogen bonding, electrostatic interactions, or ϕ-ϕ interactions. The addition of organic materials can enhance the thermal and mechanical stability of the material, which is crucial for maintaining its structure and functionality under various operational conditions, thereby ensuring high efficiency and selectivity of adsorption (Salem et al., 2022).

Eucheuma cottonii has the potential to be used as a composite for adsorbents due to its ability to easily form gels and function as a stabilizer. Carrageenan extracted from *Eucheuma cottonii*, which contains functional groups $-OH$ and $-SO_3^-$, has the ability to form strong and flexible polymer networks. Additionally, the natural porous structure of *Eucheuma cottonii* can capture and retain other molecules or particles. This includes the utilization of *Eucheuma cottonii* as a matrix in composites that combine other materials with desired adsorption properties. Therefore, with proper modification and processing, *Eucheuma cottonii* can become a promising material for the development of effective and selective adsorbents (Jumaidin et al., 2017; Khalil et al., 2017; Zhou et al., 2020; Saeed et al., 2020; Ramadhani et al., 2019).

2. EXPERIMENTAL SECTION

2.1 Chemical and Instrumental

The materials used in this study are macro algae (*Euchuema cottonii*), aluminium nitrate ($Al(NO_3)_3.9H_2O$) and nickel nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$) obtained from Sigma Aldrich, sodium hydroxide (NaOH) and sodium carbonate (Na_2CO_3) obtained from EMSURE® ACS, distilled water (H_2O), pH 10 buffer solution, cationic dyes rhodamin-b, malachite green and methylene blue, anionic dyes direct yellow, methyl orange, and direct green.

The tools used in this research are analytical balance, standard glassware including erlenmeyer, beaker, measuring cup, dropper and volumetric pipette, magnetic stirring rod, mortar, oven, hotplate, filter paper, buchner funnel and vacuum, shaker, pH meter, hydrothermal steel, and UV-Vis spectrophotometer.

2.2 Preparation of Macro Algae *Eucheuma cottonii*

Eucheuma cottonii macro algae was cleaned using distilled water. After cleaning, *Eucheuma cottonii* is dried in an oven at 105℃ to remove its moisture content. The sample is then mashed using a mortar and sieved using a 200 mesh sieve.

2.3 Modification of Ni/Al-LDH with *Eucheuma cottonii*

Modification of Ni/Al-LDH with *Eucheuma cottonii* were prepared using co-precipitation and hydrothermal techniques. Ni/Al-*Eucheuma cottonii* were prepared by reacting 30 mL of 0.75 M $Ni(NO_3)_2.6H_2O$ solution with 30 mL of 0.25 M $Al(NO_3)_3.9H_2O$ solution. The resulting mixture was then stirred for 30 minutes. Sodium hydroxide (NaOH) was gradually introduced into the solution until it reached pH 10. The mixture was then stirred for an additional 15 min at 80℃. Next, an amount of 3 g of *Eucheuma cottonii* was introduced into the mixture and stirred using a mechanical stirrer for 15 min. The solution was put into a hydrothermal steel and heated at 105℃ for 5 hours. Next, the mixture was filtered and washed with distilled water, followed by drying in an oven at 100℃ (Ahmad et al., 2023b; Oktriyanti et al., 2019).

2.4 Adsorbent Selectivity towards Cationic and Anionic dyes

Cationic dye solutions (rodhamin-b, methyl orange and methyl blue) and anionic dye solutions (direct yellow, methyl orange and direct green) with each absorbance made at 0.500 nm were mixed with 10 mL of each dye into separate beakers between cationic and anionic dyes. Each mixture of anionic dye and cationic dye was added with 0.2 g adsorbent and stirred for 80 minutes. The selective cationic and anionic dyes obtained were mixed and adsorption was carried out again by adding adsorbent. Wavelength measurements were taken using a UV-Vis spectrophotometer.

3. RESULTS AND DISCUSSION

3.1 Adsorbent Selectivity towards Cationic Dyes

The cationic dyes rhodamine-b (RB), malachite green (MG) and methylene blue (MB) were used to evaluate the selective nature of the adsorbent for adsorbing cationic dyes. The maximum wavelengths of cationic dyes RB, MG and MB were 554 nm, 617 nm and 664 nm respectively. These wavelengths were used to calculate the absorbance of each dye before and after adsorption using the adsorbent. Figure 1 can provide information that judging from the decrease in wavelength after adsorption, the malachite green (MG) dye wavelength peak drops more than the other dye wavelength peaks, which indicates that malachite green (MG) is absorbed better by the adsorbent and indicates better selectivity. The selectivity of the adsorbent to adsorb malachite green (MG) can be clarified by the adsorption percentage information which can be seen in Table 1.

Table 1. Percentage Adsorption Cationic Dye Selectivity

Dye	Adsorption (%)		
	Eucheuma cottonii	Ni/Al-LDH	Ni/Al-EC
RB	36.69	45.97	32.66
MG	64.68	66.27	78.17
MB	45.30	40.88	72.93

The dye Malachite Green exhibits the highest adsorption percentage among other dyes, reaching 78.17%, on the Ni/Al-EC adsorbent. The dye with the lowest adsorption percentage is Rhodamine-B, with a value of 32.66% on the Ni/Al-EC adsorbent. Malachite Green possesses characteristics that make it suitable for adsorption. In the pH range of 3.5 to 5, Malachite Green exhibits acidic properties, high solubility, and chromatic form (MG^+) with maximum absorption at 618 nm. However, under alkaline conditions, its structure transforms into a colorless carbinoal base, indicating that pH influences its structure and adsorption properties. The surface of LDH has numerous binding sites that can be occupied by protonation at acidic pH, enhancing the adsorption competition between H^+ ions and MG species. This suggests that LDH can function as a buffer and enhance adsorption capacity in the neutral to alkaline pH range due to increased electrostatic attraction between MG and the

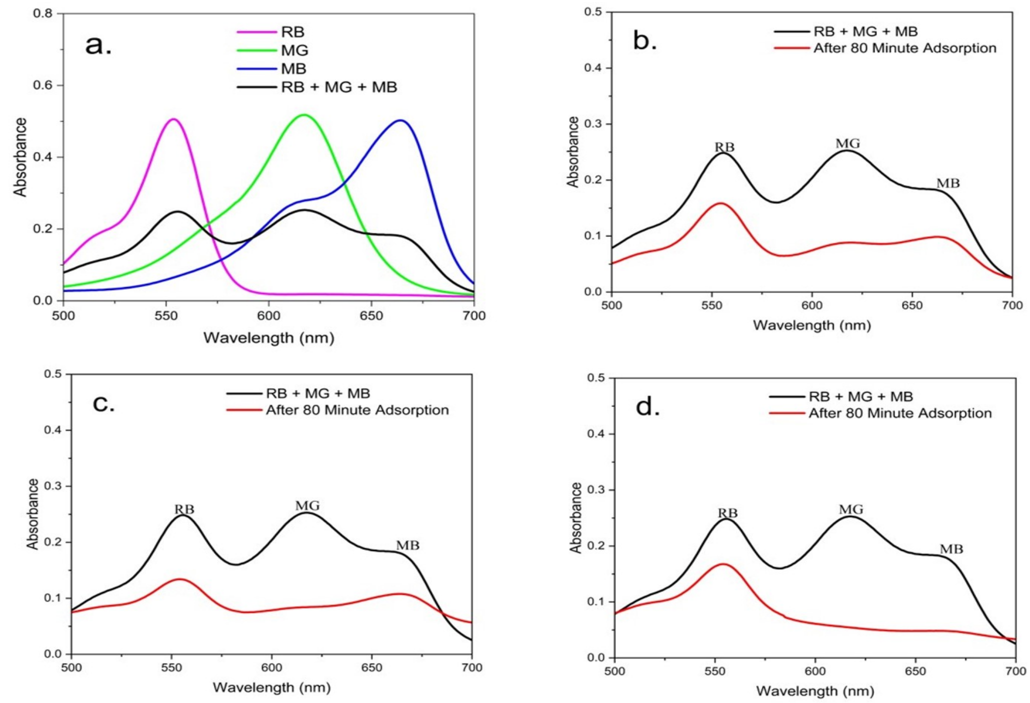

Figure 1. UV-Vis Wavelength of RB, MG, MB and Its Mixture (RB + MG + MB) (a), UV-Vis Spectra Mixture Solution (RB + MG + MB) Before and After Adsorption by EC (b), Ni/Al-LDH (c) and Ni/Al-EC (d)

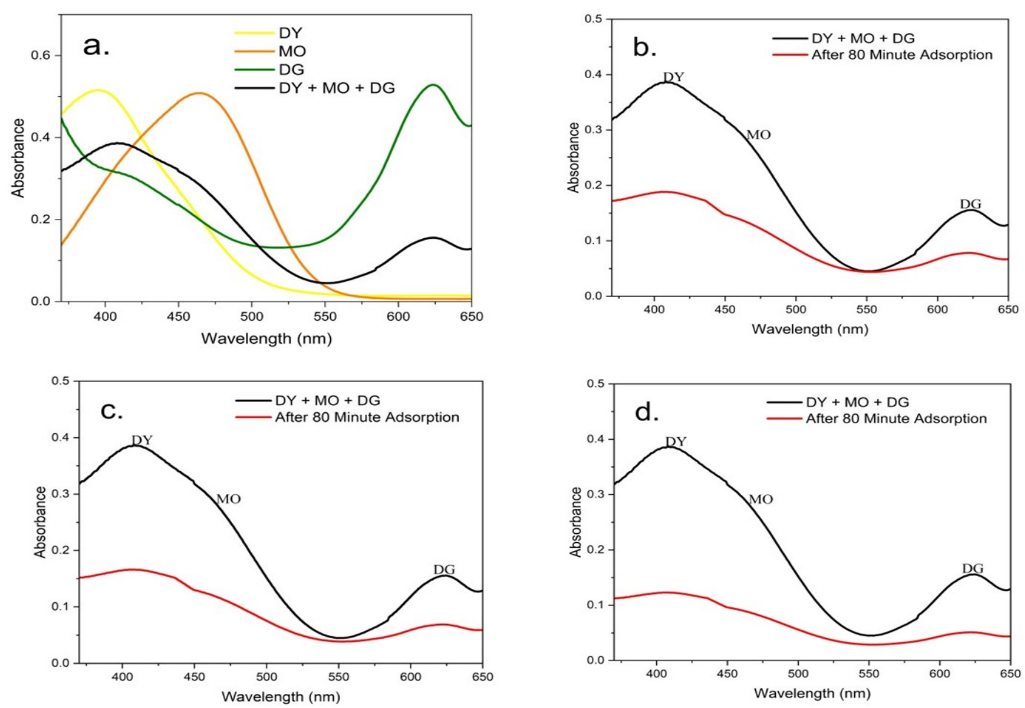

Figure 2. UV-Vis Wavelength of DY, MO, DG and Its Mixture (DY + MO + DG) (a), UV-Vis Spectra Mixture Solution (DY + MO + DG) Before and After Adsorption by EC (b), Ni/Al-LDH (c) and Ni/Al-EC (d)

adsorbent surface (Kooravand et al., 2023).

3.2 Adsorbent Selectivity towards Anionic Dyes

The anionic dyes used for selectivity are Direct Yellow (DY), Methyl Orange (MO), and Direct Green (DG). The purpose of

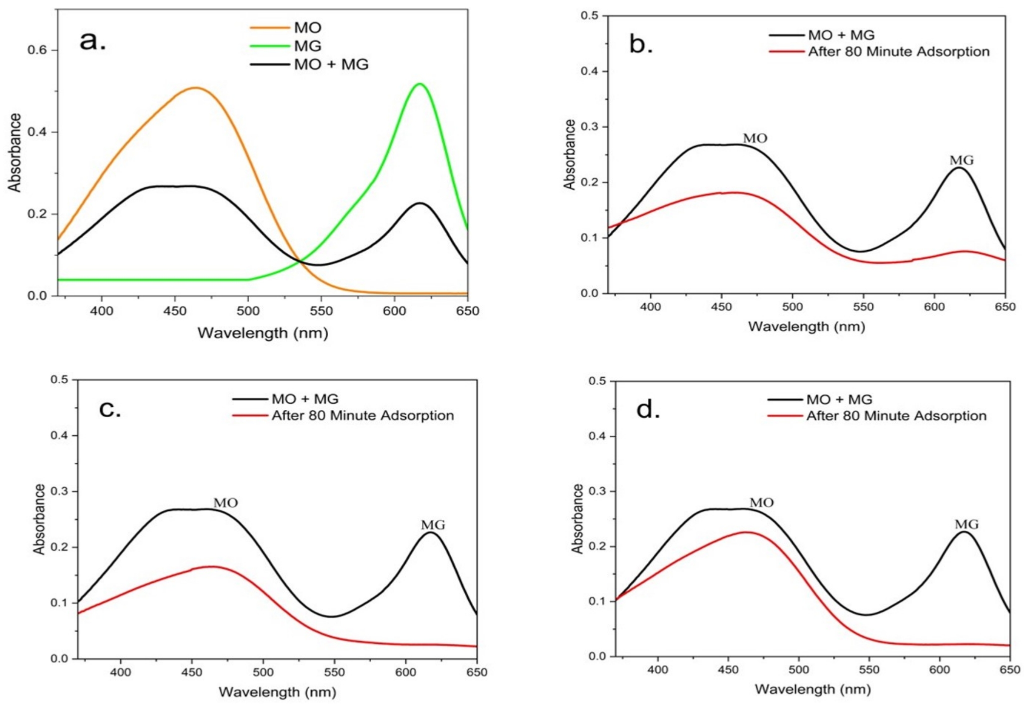

Figure 3. UV-Vis Wavelength of MO and MG and Its Mixture (MO + MG) (a), UV-Vis Spectra Mixture Solution (MO + MG) Before and After Adsorption by EC (b), Ni/Al-LDH (c) and Ni/Al-EC (d)

the selectivity treatment is to adsorb these dyes and determine the adsorbent's selectivity for anionic dyes. Measurement of the wavelength is conducted for direct yellow at 412 nm, methyl range at 464 nm, and direct green at 623 nm using the adsorbent. Before and after adsorption, the wavelength is measured to observe the reduced absorbance after the adsorption process using the adsorbent. The difference in absorbance reduction is calculated to determine the percentage of adsorption which can be seen at Table 2.

Table 2. Percentage Adsorption Anionic Dye Selectivity

Dye	Adsorption (%)		
	Eucheuma cottonii	Ni/Al-LDH	Ni/Al-EC
DY	50.26	57.29	68.23
MO	52.30	58.30	69.26
DG	40.00	54.84	67.10

The highest percentage of adsorption is found in the dye Methyl Orange with a value of 69.26%. The lowest percentage of adsorption is found in the dye Direct Green with a value of 40.00% using the *Eucheuma cottonii* adsorbent. These values correspond to the graph showing the decrease in peak wavelength, as can be seen in Figure 2.

Methyl Orange can be well adsorbed onto the adsorbent due to several specific characteristics of Methyl Orange and the interactions that occur between Methyl Orange and the adsorbent. Firstly, the ion exchange process allows Methyl Orange molecules to replace NO_3^- ions in the adsorbent. This enables more Methyl Orange molecules to enter the layers through ion exchange. The electrostatic attraction between charged Methyl Orange molecules and active sites on the adsorbent also facilitates adsorption. The physicochemical characteristics of Methyl Orange, such as molecular size and charged properties, allow effective interactions with active sites on the adsorbent (Yang et al., 2023).

3.3 Adsorbent Selectivity towards Cationic and Anionic Dyes

The cationic and anionic dyes with the highest percentage of adsorption were subjected to selective re-sorption by mixing them and then undergoing adsorption again. The cationic dye selected was Malachite Green (MG), and the most selective anionic dye was Methyl Orange (MO). The results obtained indicate that Malachite Green experiences better adsorption compared to Methyl Orange, as seen from the greater decrease in peak wavelength observed in Figure 3. Malachite Green tends to exhibit more selective adsorption on EC, Ni/Al-LDH, and Ni/Al-EC adsorbents, with respective adsorption percentage values of 66.96%, 88.99%, and 89.87% which can be seen at Table 3, with a significant difference in adsorption percentage compared to Methyl Orange.

4. CONCLUSIONS

The study successfully demonstrates the potential of using Ni/Al Layered Double Hydroxide modified with *Eucheuma cottonii* for

Table 3. Percentage Adsorption Cationic-Anionic Dye Selectivity

Dye	Adsorption (%)		
	Eucheuma cottonii	Ni/Al-LDH	Ni/Al-EC
MO	32.09	38.06	15.67
MG	66.96	88.99	89.87

the selective adsorption of both cationic and anionic dyes from solutions. The modification of the adsorbents with *Eucheuma cottonii* significantly enhances their selectivity and efficiency in removing dyes malachite green, and methyl orange. Among the tested dyes, Malachite Green showed the highest adsorption percentage, indicating a particular affinity of the modified adsorbents towards cationic dyes making them versatile agents for water purification.

5. ACKNOWLEDGEMENT

Our research were supported from Reseach Center of Inorganic Materials and Complexes Universitas Sriwijaya.

REFERENCES

Ahmad, N., F. S. Arsyad, I. Royani, and A. Lesbani (2023a). Charcoal Activated As Template Mg/Al Layered Double Hydroxide for Selective Adsorption of Direct Yellow on Anionic Dyes. *Results in Chemistry*, **5**; 100766

Ahmad, N., S. Wibiyan, I. Royani, R. Mohadi, and A. Lesbani (2023b). Reusable Heterogeneous Catalyst (M^{2+}) Al-Layered Double Hydroxide Used for Oxidative Desulfurization of 4,6-Dimethyldibenzothiophene. *Indonesian Journal of Material Research*, **1**(3); 99–105

Ahmad, N., A. Wijaya, E. S. Fitri, F. S. Arsyad, R. Mohadi, and A. Lesbani (2022). Catalytic Oxidative Desulfurization of Dibenzothiophene by Composites Based Ni/Al-Oxide. *Science and Technology Indonesia*, **7**(3); 385–391

Amri, A., A. Lesbani, and R. Mohadi (2023). Malachite Green Dye Adsorption from Aqueous Solution using a Ni/Al Layered Double Hydroxide-Graphene Oxide Composite Material. *Science and Technology Indonesia*, **8**(2); 280–287

Amri, A., S. Wibiyan, A. Wijaya, N. Ahmad, R. Mohadi, and A. Lesbani (2024). Efficient Adsorption of Methylene Blue Dye Using Ni/Al Layered Double Hydroxide-Graphene Oxide Composite. *Bulletin of Chemical Reaction Engineering & Catalysis*, **19**(2); 181–189

Bagherzadeh, M., G. Salehi, and N. Rabiee (2024). Rapid and Efficient Removal of Methylene Blue Dye from Aqueous Solutions Using Extract-Modified Zn–Al LDH. *Chemosphere*, **350**; 141011

Dai, X., C. Jing, K. Li, X. Zhang, D. Song, L. Feng, X. Liu, H. Ding, H. Ran, and K. Zhu (2023). Enhanced Bifunctional Adsorption of Anionic and Cationic Pollutants by MgAl LDH Nanosheets Modified Montmorillonite Via Acid-Salt Activation. *Applied Clay Science*, **233**; 106815

Hanifah, Y., R. Mohadi, M. Mardiyanto, N. Ahmad, S. Suheryanto, and A. Lesbani (2023). Polyoxometalate Intercalated M^{2+}/Al (M^{2+}= Ni, Mg) Layered Double Hydroxide for Degradation of Methylene Blue. *Bulletin of Chemical Reaction Engineering & Catalysis*, **18**(2); 210–221

Jumaidin, R., S. Sapuan, M. Jawaid, M. Ishak, and J. Sahari (2017). Characteristics of *Eucheuma cottonii* Waste from East Malaysia: Physical, Thermal and Chemical Composition. *European Journal of Phycology*, **52**(2); 200–207

Khalil, H., Y. Tye, C. Saurabh, C. Leh, T. Lai, E. Chong, M. Fazita, J. M. Hafiidz, A. Banerjee, and M. Syakir (2017). Biodegradable Polymer Films from Seaweed Polysaccharides: A Review on Cellulose As a Reinforcement Material. *Express Polymer Letters*, **11**(4); 244–265

Kooravand, M., H. Haddadi, S. Asadpour, S. Farhadian, N. Sarmast, and A. Asfaram (2023). Simply Synthesized Ca-Al-LDH-Thiosulfate As Adsorbent for Removal of Malachite Green from Aqueous Solution. *Polyhedron*, **246**; 116653

Mohadi, R., N. Ahmad, S. Wibiyan, Z. A. Zahara, E. S. Fitri, Mardiyanto, I. Royani, and A. Lesbani (2023). Synthesis of Zn/Al-ZnO Composite Using Zn/Al-Layered Double Hydroxide for Oxidative Desulfurization of 4-Methyldibenzothiophene. *Science and Technology Indonesia*, **8**(4); 701–709

Normah, N., N. Juleanti, P. M. S. B. N. Siregar, A. Wijaya, N. R. Palapa, T. Taher, and A. Lesbani (2021). Size Selectivity of Anionic and Cationic Dyes Using LDH Modified Adsorbent with Low-Cost Rambutan Peel to Hydrochar. *Bulletin of Chemical Reaction Engineering & Catalysis*, **16**(4); 869–880

Oktriyanti, M. M., N. R. Palapa, R. Mohadi, and A. Lesbani (2019). Modification Of Zn-Cr Layered Double Hydroxide With Keggin Ion $[\alpha\text{-SiW}_{12}O_{40}]^{4-}$ As Cr (VI) Adsorbent. *Indonesian Journal of Environmental Management and Sustainability*, **3**(3); 93–99

Ramadhani, F. S., I. Rostini, Z. Anna, and E. Rochima (2019). Characterization of Edible Film from Seaweed Flour (*Eucheuma cottonii* Weber-Van Bosse, 1913) with Different Types of Plasticizer. *World Scientific News*, **133**; 23–33

Saeed, A. A. H., N. Y. Harun, S. Sufian, A. A. Siyal, M. Zulfiqar, M. R. Bilad, A. Vagananthan, A. Al-Fakih, A. A. S. Ghaleb, and N. Almahbashi (2020). *Eucheuma cottonii* Seaweed-Based Biochar for Adsorption of Methylene Blue Dye. *Sustainability*, **12**(24); 10318

Salem, M. A., A. M. Khan, Y. K. Manea, and A. A. Wani (2022). Nano Chromium Embedded in f-CNT Supported CoBi-LDH Nanocomposites for Selective Adsorption of Pb^{2+} and Hazardous Organic Dyes. *Chemosphere*, **289**; 133073

Siregar, P. M. S. B. N., N. R. Palapa, A. Wijaya, E. S. Fitri, and A. Lesbani (2021). Structural Stability of Ni/Al Layered Double Hydroxide Supported on Graphite and Biochar toward Adsorption of Congo Red. *Science and Technology Indonesia*, **6**(2); 85–95

Yang, L., T. Huiyuan, X. Mengyan, C. Baoyu, L. Chang, D. Xiuhong, W. Zehua, D. Xianying, and C. Jiehu (2023). Synergistic Removal of Mixed Methyl Orange/Sunset Yellow Solution by the Graded ZnCrNi-LDHs Porous Material. *Arabian Journal of Chemistry*, **16**(10); 105163

Zahara, Z. A., I. Royani, N. R. Palapa, R. Mohadi, and A. Lesbani (2023). Treatment of Methylene Blue Using Ni-Al/Magnetite Biochar Layered Double Hydroxides Composite by Adsorption. *Bulletin of Chemical Reaction Engineering & Catalysis*, **18**(4); 659–674

Zhou, D., G. Xie, X. Hu, X. Cai, Y. Zhao, X. Hu, Q. Jin, X. Fu, X. Tan, and C. Liang (2020). Coupling of *kenaf* Biochar and Magnetic $BiFeO_3$ onto Cross-Linked Chitosan for Enhancing Separation Performance and Cr (VI) Ions Removal Efficiency. *International Journal of Environmental Research and Public Health*, **17**(3); 788

