Cationic Dye Removal By Magnesium Aluminum-Biochar Composite From Aqueous Solution

Arini Fousty Badri, Neza Rahayu Palapa, Risfidian Mohadi, Mardiyanto, Aldes Lesbani

Abstract—In this work, MgAl/BC composite has been successfully prepared and applied as efficient adsorbent of cationic dyes such as MB and RhB. The XRD properties of adsorbent shows that the presents the characterization of starting materials. The adsorption of MB and RhB was evaluated and it follows pseudo-second-order kinetic model. The adsorption study suggested Langmuir isotherm was suitable for adsorption of MB and RhB onto MgAl/BC composite with a maximum adsorption capacity up to 91.441 and 69.231 mg/g, respectively. The thermodynamic study indicates that the adsorption process is physisorption, spontaneous, and endothermic process. The regeneration study showed that three cycle adsorption process using MgAl/BC composite still has high efficiency, which confirmed that the material can be reused for further adsorption process.

Index Terms— Dye Removal, Adsorption Study, Rodhamine-B, Methylene blue, Layered Double Hydroxide, and Biochar.

1 Introduction

Reactive dyes wastewater cause polution which endanger human living and environments, before the dyes discharged into the surrounding its should be removed with effective mothode [1]. Many methodes such as ion exchange, oxidation, flocculation, precipitation reverse osmosis and adsorption were applied to removal the reactive dyes pollution[2]. By the reason of simple equipment requirement, low budget operating cost and low secondary pollution, adsorption is considered as an effective method compared from all the methodes [3]. Past researches have been expanded many adsorbents such as graphene oxide[4], chitosan[5], algae[6], zeolite nanostructures [7], bentonite [8], and layered double hydroxide [9]. Layered double hydroxides (LDH) is is a type of cationic clay materials also known as hydroxycarbonates compounds, It's have positively charged metal-hydroxide anions and the internal species in the interlayer anions can be rather easily exchange [10]. However, LDH have been studied as removal agent for dye, but the adsorption capacity has deficient adsorption capacity to cationic dyes [11]. Therefore, LDH needs to modify by means of composite method or intercalation method in order to enhance their adsorption capacity [12]. Recently, LDH composite to biochar make a new methode to make economical and effectivet adsorbent to remove many kind of pollutants. Zhang et al [13] studied MgAl LDH by co-precipitated onto the biochar matrix to remove phosphate ion from water with adsorption capacity (410 mg/g). Wang et al [14] reported arsenic removal by using reusability of NiMn-LDH and NiMn LDH composite biochar. Meili et al. [15] studied MgAl LDH composite on bone-biochar with various molar ratio (2:1, 3:1, and 4:1). The result showed that MgAl LDH composite biochar with molar ratio 2:1 and 3:1could were the best adsorbent to remove MB compared to pristine. Previous research showed that the composites of biochar with LDH is a supreme approach to enhanced adsorption capacity with high performance materials. Thus, the composite material using rice husk biochar has a potential to produce adsorbents. However, in this study, the MgAl/BC was synthesis by co-precipitated to remove methylene blue and rodhamine-B removal. The adsorption variable was determined and calculated on to several parameter adsorption such as kinetics, isotherm and thermodynamic parameters. The regeneration study determined in order to exhibited the effectivity of MgAl/BC to remove MB and RhB.

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2 Experimental Section

The chemicals used in this work including $Mg(NO_3)_2.6H_2O$, $Al(NO_3)_3.9H_2O$, NaOH and HCl were obtained from Sigma Adrich and Merck. Biochar were obtained from local paddy field in Indonesia. The characterization were analyses by XRD and FTIR. The concentration of dye was analyzed using UV-Visible spectrophotometer Bio-Base BK-UV1800 at wavelength of maximum absorbance for MB 664nm, MG 617 nm and RhB 554.2 nm.

2.1 Synthesis Mg/Al LDHs

Mg/Al LDHs were synthesized based on with slightly modification [16] as follows. $Mg(NO_3)_2.6H_2O$ (0.75 M in 100 mL) and $Al(NO_3)_3.9H_2O$ (0.25 M in 100 mL) were diluted. The mixing solution added dropwise into 0.05 L of 3 M NaOH then stirred for 2 hours keep at pH 10. Furthermore, the mixing solution was heated at 60 ^oC for 24 hours to form Mg/Al LDHs.

2.2 Preparation Mg/Al LDH composite to biochar

Synthesis of Zn-Cr LDH was conducted by coprecipitation method. Zinc(II) nitrate (0.1 L, 0.5 M) was mixed with chromium(III) nitrate (0.1 L, 0.1 M). The mixture was constantly stirred and sodium carbonate (50 mL, 2.5 M) was added to the mixture following with addition of sodium hydroxide (3 M) until pH 10. Reaction was kept at 70 ^oC for 24 hours to form solid material. Solid material was filtered, washed with water several times, and dried at 110 ^oC.

2.3 Adsorption Experiment Procedures

As much as 0.05 g of adsorbents was added into 20 mL of RhB and MB, respectively, containing solution with continuous stirring over a magnetic stirrer at 230 rpm. All experiments were conducted in twice counts. For a predetermined times interval, ranging 5 until 200 mins, various initial concentration and adsorption temperature, the dye adsorbed were counts and determining by kinetics models, isotherm and thermodynamic parameters. The removal capacity qe (mg/g) was calculated with Equations (1)

$$qe = \frac{(Co - Ce).V}{W} \quad (1)$$

where Co is the initial concentration of cationic dyes (mg/L), Ce is the equilibrium or residual dye concentration (mg/L), V is the volume of the dye solution (L), and W is the mass of adsorbent (g). Furthermore, the adsorption kinetics parameter examined using pseudo-first-order and pseudo-second-order model as described in the following equation (2) and (3).

$$\log (Q_e - Q_t) = \log Q_e \ (k_1/2.303) \quad (2)$$
$$t/Q_t = (1/k_2 Q_e^2) + (1/Q_e)\ t \quad (3)$$

Q is the adsorption capacity (e is equilibrium state and t is variable of time state), k is kinetics adsorption rate of kinetic models. Next, isotherm parameters were calculated based on the Langmuir and Freundlich equations as follows equation (4) and (5):

$$C_e/Q_e = (C_e/Q_m) + (1/Q_m k_L) \quad (4)$$
$$\text{Log } Q_e = \log k_F + 1/n \log C_e \quad (5)$$

C is dye concentration, Qmax is adsorption maxmum capacity, K is constant of isotherm model and n is freedom of isotherm. The desorption experiment was carried out with water, hot water, acetone, HCl and NaOH. 0.5 g adsorbent adsorbed cationic dyes was added to 20 mL several eluents (0.01 M), the solution was stirred for 90 min. Then measured the concentration of dyes desorbed. The desorption process was repeated for each adsorbent. The adsorbent was dried and used in the next adsorption process called regeneration.

3 Results and Discussion

Characterization of MgAl LDH, BC and MgAl/BC LDH composite was analyzed by XRD. Fig. 1. (a) exhibited the intense diffraction of MgAl LDH at 11.81° (003) with interlayer space is 7.71 Å. The other characteristic peaks of MgAl LDH material appear at plane (006), (012), (110) and (116). Fig. 1. (b) showed the presence of reflection (002) consist of the broad peak amorphous indicated the silicate carbon amorphous from rice husk biochar. The XRD pattern of MgAl/BC composite LDH shown in Fig. 1. (c). The pattern of composite material showed the presence of both characteristic of raw material (MgAl LDH and biochar). The interlayer of MgAl/BC LDH composite increased slightly to 8.31 Å and indicated the biochar was composited and intercalated in interlayer. Similar reported by Zubair *et al* [17] assumed that the increasing interlayer attributed to the agglomeration from the loading of biochar into interlayers of LDH. However, MgAl/BC LDH composite was observed may result in reduce of LDH crystallinity associated with a reduction in peak intensity.

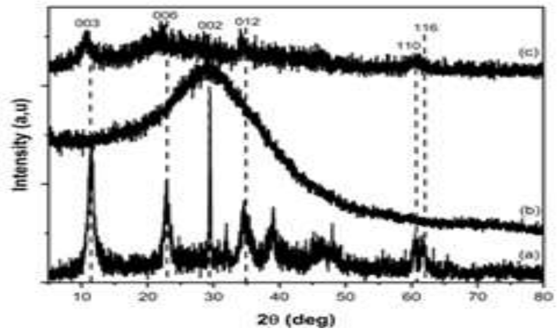

Fig. 1 X-ray diffraction of (a) MgAl LDH (b) BC and (c) MgAl/BC LDH composite

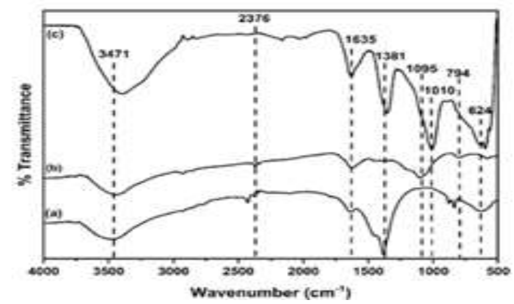

Fig. 2 FT-IR Spectrum of (a) MgAl LDH (b) BC and (c) MgAl/BC LDH composite

The effect of adsorption time on the adsorption of RhB and MB into MgAl and MgAl/BC composite was examined using time contact variable. 50 mg of MgAl and MgAl/BC composite was added into 0.05 L of adsorbate concentration 30 mg/L. The mixture was stirred using horizontal shaker with time variations of 0, 5, 10, 15, 20, 50, 60, 70, 90, 120, 150, 180 and 200 minutes. RhB and MB adsorption results were shown in Fig. 3.

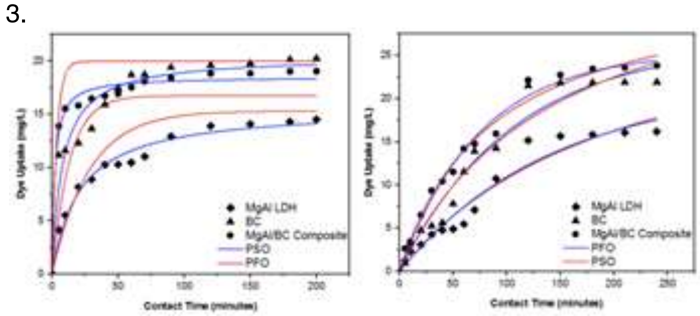

Fig. 3 Time variation of adsorption of (a) RhB and (b) MB onto MgAl LDH, BC and MgAl/BC composite

Fig. 3 shows that the dye uptake increased rapidly with time before reaching equilibrium. MgAl LDH reaches equilibrium in 90 minutes, BC in 70 minutes and MgAl/BC in 60 minutes for RhB adsorption. MB adsorption onto MgAl, BC and MgAl/BC were reached equlibrium after 100 minutes. Furthermore, the increase of adsorption capacity caused by the driving force of the concentration gradient [18]. Fig. 2 shows the kinetic model of CR removal by various adsorbents. However, the RhB adsorbed onto BC higher than MgAl composite, when, MB adsorbed onto MgAl composite higher than BC. This phenom described in Fig. 3. Fig 3 showed the competition of MB and RhB adsorption using MgAl/BC composite material.

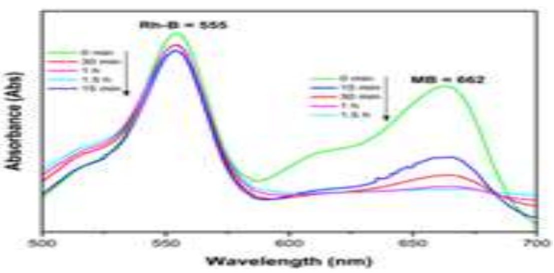

Fig. 4 Dye molecule compitition adsorption onto MgAl/BC composite

Fig 4. Denoted that the MB adsorption onto MgAl/BC composite had been efficient than RhB for continous times adsorption. This caused that the bigger molecules of RhB caused that the adsorption become hard and the efficiency of adsorption capacity was equilibrium for MgAl/BC composite. the chemical structure of MB and RhB were presents in Fig. 5.

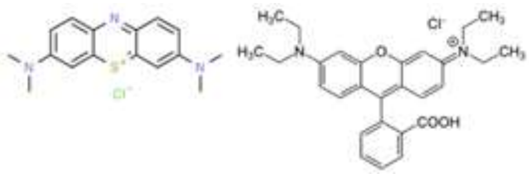

Fig. 5 the structure of (a) Methylene Blue (MB) and (b) Rhodamine-B (RhB)

The parameters and correlation coefficients (R^2) acquired from linear plotting log(qe-qt) vs t (PFO) and t/qt vs t (PSO) were listed in Table 1. In all cases, the result shows based on R^2 >0.890 that PSO is preferred then PFO. This finding supported by the $qe_{(calc)}$ PSO which is close to the $qe_{(exp).}$ This result represented that the adsorption follows PSO kinetic model, which represents that electrostatic attraction from mixing adsorbate-adsorbent. Additionally, the increasing k_2 values after composites reflected in the faster time needed by the respective systems to achieve equilibrium.

Table 1 Kinetic parameters of dyes adsorption onto Mg/Al-LDH and MgAl/BC Composite

	PFO			PSO		
Co (mg/L)	qe (mg/g)	K_1 (min^{-1})	R2	qe(mg/g)	K_2(g mg min^{-1})	R2
100	8.156	0.009	0.875	14.925	0.0003	0.890
100	11.329	0.012	0.930	21.052	0.0002	0.968
100	13.941	0.020	0.931	16.286	0.0007	0.976
20	6.140	0.023	0.902	8.026	0.005	0.994
20	5.551	0.028	0.953	9.470	0.010	0.997
20	4.004	0.030	0.931	9.737	0.021	0.999

The variation of temperature was determined to adsorption capacities from material due to adsorption mechanism. 50 mg of adsorbents was added into 0.05 L of adsorbate in various initial concentrations and temperature. The study of effectivity of dyes concentration and temperature to the adsorption capacity of RhB and MB onto MgAl/BC composite can be seen in Fig. 6.

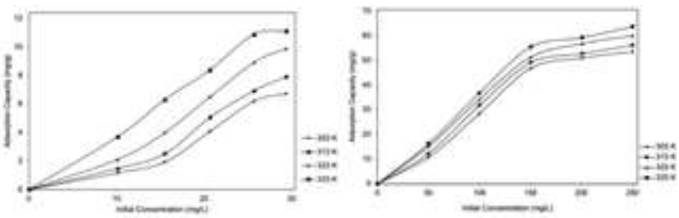

Fig. 6 Equilibrium state of (a) RhB and (b) MB removal onto MgAl/BC composite

Fig. 6 showed that the obtained graph indicated that MgAl/BC composite has the largest adsorption capacity of MB (62.32 mg/g) than RhB (11.56 mg/g). The isotherm model was determined in order to analyze the adsorption process by Freundlich and Langmuir. The Freundlich isotherm adsorption model usually describes multilayer process in heterogeneous surface and the Langmuir isotherm is also describe the interaction of adsorbent-adsorbate which extent in one layer or one site occupied in the homogeneous surface [19]. The results were listed in Table 2. Table 2 showed the isotherm adsorption model such as Langmuir and Freundlich. The data confirm that the adsorption process follows Langmuir isotherm models and explained that the adsorption process is monolayer.

Table 2 Isotherms Parameter of Adsorption Rhodamine B onto Mg/Al-LDH and MgAl/BC Composite

Dyes	adsorption isotherm	adsorption constant	
RhB	Langmuir	Qmax	38.496
		k1	0.002
		R2	0.959
	Freundlich	N	1.087
		Kf	5.840
		R2	0.913
MB	Langmuir	Qmax	91.444
		k1	0.310
		R2	0.926
	Freundlich	N	0.457
		Kf	1.004
		R2	0.837

The thermodynamic data for the adsorption of RhB and MB onto MgAl/BC composite presents in Tables 3. Based on data in Tables 3, the adsorption process of RhB and MB onto MgAl/BC composite occurred spontaneously. Furthermore, the enthalpy indicated that the adsorption process has low energy and interaction of materials and adsorbate is only low interaction. It also can be observed that the adsorption process more favorable.

Table 3 Thermodynamic parameters of Adsorption RhB and MB onto MgAl/BC Composite

T (K)	Dye	△H (kJ/mol)	△S (kJ/mol)	△G (kJ/mol)
303	RhB	13.571	0.056	-3.471

313				-4.034
323				-4.596
333				-5.159
303		13.571	0.056	-3.471
313	MB			-4.034
323				-4.596
333				-5.159

The desorption process was determined in order to examine about the molecule escapes from surface site of adsorbent [20]. In our study, desorbed material were conducted by several reagents to examine a stability of material or the material can be reused. Fig 7 presents the desorption study of RhB and MB in several adsorbents. The largest percentage of desorption of RhB was in the HCl solvent onto MgAl 86.95% and the MgAl/BC and BC the largest desorption in NaOH as much as 73.11 and 13.84%. we assumed the uses of acidic reagents, MgAl LDH can be exfoliated so the molecules that were interaction into surface site of the material would be easily desorbed. vice versa, in base solution, the dye molecule become negatively charge, meanwhile, the surface charge of BC and MgAl composite become negatively too.

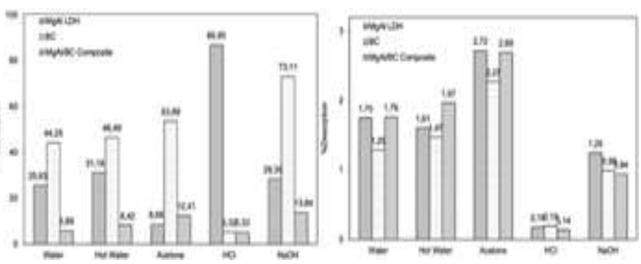

Fig. 7 Desorption RhB (a) and MB (b) on Mg/Al-LDH, BC and on MgAl/BC Composite

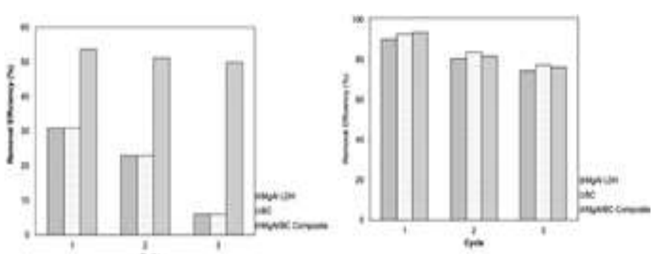

Fig. 8 Regeneration RhB (a) and MB (b) on Mg/Al-LDH, BC and on MgAl/BC Composite

Fig. 8 presents after three cycles of adsorption-desorption. Fig. 8 a showed the efficiency of dye removal decreased extreamely for MgAl and BC, otherwise, MgAl/BC composite exhibited the stability adsorption in regeneration process. Fig 8.b. showed the continuously adsorption in regeneration process. The adsorption after third cycle seems stability.

4 Conclusion

In this work, MgAl/BC composite has been successfully prepared and applied as efficient adsorbent of cationic dyes such as MB and RhB. The XRD properties of adsorbent shows that the presents the characterization of starting materials. This material used as an adsorbent to remove MB and RhB. The parameters of adsorption were determined using kinetic, isotherm, and thermodynamic parameters. The kinetic model of pseudo-second-order was fitted for the composite material with $q_{e\ calculation}$ closed to $q_{e\ experiment}$. Isotherm study of MgAl/BC composite suggest the adsorption follows Langmuir model through monolayer adsorption process with maximum capacity up to 91.441 and 69.231 mg/g for MB and RhB, respectively. The thermodynamic analysis indicates that adsorption in all adsorbents was spontaneous (ΔG<0) and endothermic. Futhermore, the regeneration study concluded that after three cycles adsorption process, the adsorbent shows high efficiency and can be reused for cationic dyes adsorption in aqueous solution.

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References

[1] T. Robinson, G. McMullan, R. Marchant, and P. Nigam, “Remediation of dyes in textile effluent: A critical review on current treatment technologies with a proposed alternative,” Bioresour. Technol., vol. 77, no. 3, pp. 247–255, 2001.

[2] J. A. Oliveira, F. A. Cunha, and L. A. M. Ruotolo, “Synthesis of zeolite from sugarcane bagasse fly ash and its application as a low-cost adsorbent to remove heavy metals,” J. Clean. Prod., vol. 229, pp. 956–963, 2019.

[3] O. Segun Esan, “The Removal of Single and Binary Basic Dyes from Synthetic Wastewater Using Bentonite Clay Adsorbent,” Am. J. Polym. Sci. Technol., vol. 5, no. 1, p. 16, 2019.

[4] M. Rajabi, K. Mahanpoor, and O. Moradi, “Preparation of PMMA/GO and PMMA/GO-Fe 3 O 4 nanocomposites for malachite green dye adsorption: Kinetic and thermodynamic studies,” Compos. Part B Eng., vol. 167, pp. 544–555, 2019.

[5] C. Zubieta, M. B. Sierra, M. A. Morini, P. C. Schulz, L. Albertengo, and M. S. Rodŕguez, “The adsorption of dyes used in the textile industry on mesoporous materials,” Colloid Polym. Sci., vol. 286, no. 4, pp. 377–384, 2008.

[6] R. Foroutan, R. Mohammadi, J. Razeghi, and B. Ramavandi, “Performance of algal activated carbon/Fe 3 O 4 magnetic composite for cationic dyes removal from aqueous solutions,” Algal Res., vol. 40, no. January, p. 101509, 2019.

[7] E. Erdem, N. Karapinar, and R. Donat, “The removal of heavy metal cations by natural zeolites,” J. Colloid Interface Sci., vol. 280, no. 2, pp. 309–314, 2004.

[8] T. Taher, R. Mohadi, D. Rohendi, and A. Lesbani, “Kinetic and thermodynamic adsorption studies of congo red on bentonite,” AIP Conf. Proc., vol. 1823, 2017.

[9] H. Starukh and S. Levytska, “The simultaneous anionic and cationic dyes removal with Zn–Al layered double hydroxides,” Appl. Clay Sci., vol. 180, no. June, pp. 0–5, 2019.

[10] T. Takei, A. Miura, and N. Kumada, “Soft-chemical

synthesis and catalytic activity of Ni-Al and Co-Al layered double hydroxides (LDHs) intercalated with anions with different charge density," J. Asian Ceram. Soc., vol. 2, no. 3, pp. 289–296, 2014.

[11] R. Elmoubarki et al., "Ni/Fe and Mg/Fe layered double hydroxides and their calcined derivatives: Preparation, characterization and application on textile dyes removal," J. Mater. Res. Technol., vol. 6, no. 3, pp. 271–283, 2017.

[12] M. S. Zoromba, M. A. Nour, H. E. Eltamimy, and S. A. Abd El-Maksoud, "Effect of modified layered double hydroxide on the flammability and mechanical properties of polypropylene," Sci. Eng. Compos. Mater., vol. 25, no. 1, pp. 101–108, 2018.

[13] M. Zhang and B. Gao, "Removal of arsenic , methylene blue , and phosphate by biochar / AlOOH nanocomposite," Chem. Eng. J., vol. 226, pp. 286–292, 2013.

[14] S. Wang, B. Gao, Y. Li, A. R. Zimmerman, and X. Cao, "Sorption of arsenic onto Ni/Fe layered double hydroxide (LDH)-biochar composites," RSC Adv., vol. 6, no. 22, pp. 17792–17799, 2016.

[15] L. Meili et al., "MgAl-LDH/Biochar composites for methylene blue removal by adsorption," Appl. Clay Sci., vol. 168, no. May 2018, pp. 11–20, 2019.

[16] M. Djellali, P. Aranda, and E. Ruiz-Hitzky, "Silica-layered double hydroxide nanoarchitectured materials," Appl. Clay Sci., vol. 171, no. January, pp. 65–73, 2019.

[17] M. Zubair, M. Daud, G. McKay, F. Shehzad, and M. A. Al-Harthi, "Recent progress in layered double hydroxides (LDH)-containing hybrids as adsorbents for water remediation," Appl. Clay Sci., vol. 143, no. March, pp. 279–292, 2017.

[18] N. R. Palapa, R. Mohadi, A. Rachmat, and A. Lesbani, "Adsorption Study of Malachite Green Removal from Aqueous Solution Using Cu / M 3 + (M 3 + = Al , Cr) Layered Double Hydroxide," Mediterr. J. Chem., vol. 10, no. 1, pp. 33–45, 2020.

[19] S. Chilukoti and T. Thangavel, "Enhanced adsorption of Congo red on microwave synthesized layered Zn-Al double hydroxides and its adsorption behaviour using mixture of dyes from aqueous solution," Inorg. Chem. Commun., vol. 100, no. December 2018, pp. 107–117, 2019.

[20] L. B. Escudero, E. Agostini, and G. L. Dotto, "Application of tobacco hairy roots for the removal of malachite green from aqueous solutions: Experimental design, kinetic, equilibrium, and thermodynamic studies," Chem. Eng. Commun., vol. 205, no. 1, pp. 122–133, 2018.