

MAGNETISM EFFECT ONTO ALUMINA TOWARDS THE MALACHITE GREEN REMOVAL IN AQUEOUS SOLUTION

Northaqifah Hasna Mohamed Khir¹, Nur Fatien Muhamad Salleh², Aina Sofiya Mahat³, Nurqasrina Iffah Ruslan³, Mohd Shahrul Nizam Salleh³, and Adibah Mohd Noor⁴

¹Faculty of Applied Sciences, Universiti Teknologi MARA, Terengganu Branch, Bukit Besi Campus
23200 Bukit Besi, Terengganu, Malaysia.

²School of Health Sciences, Universiti Sains Malaysia, Health Campus,
16150 Kubang Kerian, Kelantan, Malaysia.

³College of Chemical Engineering, Universiti Teknologi MARA, Terengganu Branch, Bukit Besi Campus
23200 Bukit Besi, Terengganu, Malaysia.

⁴Faculty of Applied Sciences, Universiti Teknologi MARA, Perak Branch, Tapah Campus
35400 Tapah Road, Perak, Malaysia.

¹hasnakhir@gmail.com, ⁴adibah_mnoor@uitm.edu.my

ABSTRACT

Removal of hazardous effluents from the wastewater is crucial for sustainable effluent management. Since industrial activities keep rising to meet the global demand, it is a major concern to monitor the waste management to protect our environment. Dyes and heavy metals are major effluents coming from the industries. Despite other technologies, the ability of magnetic alumina to adsorb one of the carcinogenic dyes, malachite green in an aqueous solution was investigated as an alternative adsorbent due to its low cost, ease of find and higher binding capacities. The synthesized adsorbents were categorized into three different magnetism compounds giving three composites of CoAl, FeAl and NiAl. Chemical characterization using KBr FTIR indicates the presence of hydroxyl groups, alumina and metal stretching in the structure of the magnetic alumina for all composites. The adsorption of malachite green was conducted with a variation contact time of 15–180 min. Malachite green was best removed by FeAl at 90 minutes with 97% percent removal.

Keywords: malachite green, adsorption, removal, magnetism, alumina

1.0 INTRODUCTION

Malachite green (MG); a highly water soluble synthetic triarylmethane dye is commonly utilized in aquaculture as a parasiticide and fungicide as well in food, textile, and health industries [2]. Figure 1 shows that MG has a complex molecular structure that is highly stable, non-biodegradable, resists light and oxidizing chemicals. The MG discharges give an adverse impact on the visual quality of water bodies, and it interferes with the life cycles of aquatic organisms by reducing the penetration of sunlight into the water. Consequently, photosynthesis and plant growth will be disturbed and influence the biological activity of aquatic animals by interfering with the physiology of the pituitary liver, gills, kidneys, intestines, gonads, and gonad vegetative cells. Additionally, the synthetic dyes present in MG are toxic to humans, mutagenic and affect to the immune and reproductive systems.

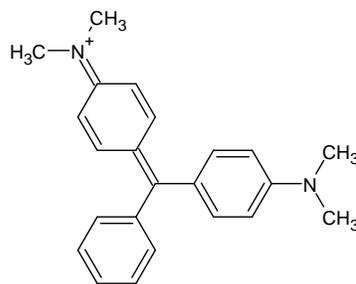


Figure 1. Chemical structure of malachite green

Inhaling MG can cause respiratory system inflammation while ingesting it can cause digestive tract irritation [3]. The dye may be transformed into leucomalachite green and carbinol which are harmful to humans. The half-life of MG in fish muscles, fat, and internal organs is ten days. This cationic dye is similarly long-lasting in the environment, having a half-life of 12.9 - 50.34 days in sediment. Some countries have reduced the usage of MG as toxicological risks become a major concern. The dye is a probable carcinogen, tends to stay in the environment, and hazardous to the aquatic and terrestrial creatures [4].

Since dyes are poorly degradable contaminants which are carcinogenic to human health and aquatic life, removal techniques have been developed to reduce the contamination of dyes in wastewater. The implementation techniques include lime precipitation, ion exchange, membrane processing, adsorption and electrolytic processes. Nevertheless, it is important to acknowledge that these methods have certain limitations. However, these methods face limitations due to high capital and operational costs and are associated with secondary waste generation. Among these approaches, adsorption is considered as economical, environmentally favourable, sustainable, fast and it promisingly being as an extensive application [5].

Environmentally stable adsorbent such as activated aluminium oxide or alumina has been used for the removal of Diresul Black, which is a dye used in the textile processing industry [6]. Utilizing the magnetism properties compound to an adsorbent is highly desirable to increase the adsorption capacity [7]. Within the scope of this study, alumina is coated with magnetism compounds of cobalt, ferum and nickel producing CoAl, FeAl and NiAl accordingly.

The objective was to synthesize nanomagnetic alumina adsorbents by loading iron (Fe), cobalt (Co), and nickel (Ni) metal onto alumina and to investigate its efficacy in removing malachite green from aqueous solutions. The adsorbents were then characterized using Fourier-transform infrared spectroscopy (FTIR).

2.0 METHODOLOGY

2.1 Chemicals

Aluminium oxide (Al_2O_3), cobalt (II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), iron (III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), nickel (II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and malachite green were purchased from Merck. All reagents were of analytical grade purity and were used as received. The water solvents used were laboratory-made distilled water and deionized water.

2.2 Preparation of Magnetic Alumina as Adsorbent

Magnetic alumina was used as an adsorbent to remove the malachite green from the aqueous solution. In this study, the magnetic alumina was prepared by coating the alumina with three different magnetism compounds of cobalt (Co), iron (Fe) and nickel (Ni) and was labelled as CoAl, FeAl and NiAl accordingly.

For the preparation of magnetic alumina, 2 g alumina was stirred in 20 mL of deionized water will at 40°C for 10 minutes. At the same time, 5 wt % of cobalt (II) nitrate hexahydrate was be added into 35 mL of deionized water forming homogeneous Co mixture. The Co mixture was poured into alumina beaker and stirred at 80 °C for 3 hours and then dried at 100 °C for 2 hours in the oven. The dried powder was then calcined at 550 °C for 3 hours. The product was then stored in a centrifuge tube upon adsorption process.

The preparation of another two magnetic alumina with Fe and Ni as the coating compound follows the same procedures as CoAl.

2.3 Characterization of Magnetic Alumina

The characterization of the potential adsorbent before and after the adsorption was performed using Fourier-transform infrared spectroscopy (FT-IR) within a scan range of 400–4000 cm⁻¹ of the FTIR Bruker Tensor 27 Spectrometer. FTIR KBr pellet technique was used for identifying functional groups of the composites. The composites were mixed with KBr at ratio 1:10 before being grounded into powder. Then, the powder mixture was placed on a pellet disc with diameter 13 mm and compressed in a hydraulic press 7000 psi for 5 minutes to form a thin pellet.

2.4 Batch Adsorption Study

Stock solution of 1000 mg/L was prepared by dissolving the malachite green in deionized water. Various concentrations of working solutions were then prepared for adsorption by diluting the stock solution in appropriate percentages.

A batch adsorption system was studied to assess the influence of nine contact times (15, 30, 60, 75, 90, 120, 150, 180, 210 minutes) on malachite green (MG) adsorption. 0.1 g of each CoAl, FeAl and NiAl were added in three different 250 mL beakers containing 200 mL of a 25 mg/L MG solution. The solution was stirred using a magnetic stirrer until it reached the equilibrium state. 15 mL was then withdrawn from the solution at a predetermined time interval into the centrifuge tube. The solution was then centrifuged upon analysis. The adsorption process for all adsorbents was replicated three times.

To determine the concentration of MG before and after the adsorption process, a handheld colorimeter by Hach DR900 was used at a wavelength of 610 nm.

2.5 Adsorption Calculation

The calibration series of MG solutions gave a straight-line curve with R² = 0.9952. The removal percentage of MG were calculated by using the following equation:

$$\text{Removal percentage (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

where C₀ and C_e are the concentration of initial and after adsorption respectively (mg L⁻¹).

3.0 RESULTS AND DISCUSSION

The synthesized adsorbents: CoAl, FeAl and NiAl were chemically characterized using KBr FTIR and analyzed. Meanwhile, the removal of MG in aqueous solution was conducted with the influence of contact time parameter. The best potential adsorbent was selected in accordance with the highest removal percentage of MG. Again, the potential adsorbent was characterized using FTIR to observe the presence of malachite green in the adsorbent after the removal.

3.1 FT-IR Studies of Magnetic Alumina

The IR spectra of the three adsorbents was illustrated in Figure 2. All composites showed bands associated with O-H stretching peak at 3418 cm^{-1} due to intermolecular and intramolecular hydrogen bonding on the adsorbent surface [8,9]. Bands associated with Al-O-Al at 432 cm^{-1} and metal (M-O-M) stretching in the range of $656\text{--}581\text{ cm}^{-1}$ were observed in the composites. The presence of -OH functional group could increase the adsorption percentage [10]. Slightly broader bands of Al-OH observed for FeAl indicating the composite as the best potential adsorbents compared to NiAl and CoAl. The Al (γ Al-O) peak was identified at 455 cm^{-1} while the metal (M-O-M) stretching was assigned to the region at approximately $657\text{--}586\text{ cm}^{-1}$ [11]. The band intensified highest for FeAl, which explains the Fe loading in the composites increase the dealumination of Al and isomorphous substitution of the metal which could be due to the Al-O-Al conversion to Al-O-M. Meanwhile, isomorphous substitution of Fe/Co/Ni ions with hydrogen atoms from Al_2O_3 hydroxyl nests produced Al-O-M species [12].

There is a clear indication as illustrated in Figure 2, that adsorption of MG onto FeAl had taken place, and new bonds were formed between MG and FeAl. It was observed that FeAl-MG exhibited bands that correspond to the C=C stretching of the benzene rings at 1632 cm^{-1} . The peaks revealed the -OH stretching at 3418 cm^{-1} becomes slightly broader after adsorption due the interaction between framework of the adsorbents and MG with the presence of -OH and -NH group [13]. The M-O-M band in the range $656\text{--}581\text{ cm}^{-1}$ also decreased in intensity due to the isomorphous substitution of MG in the composites.

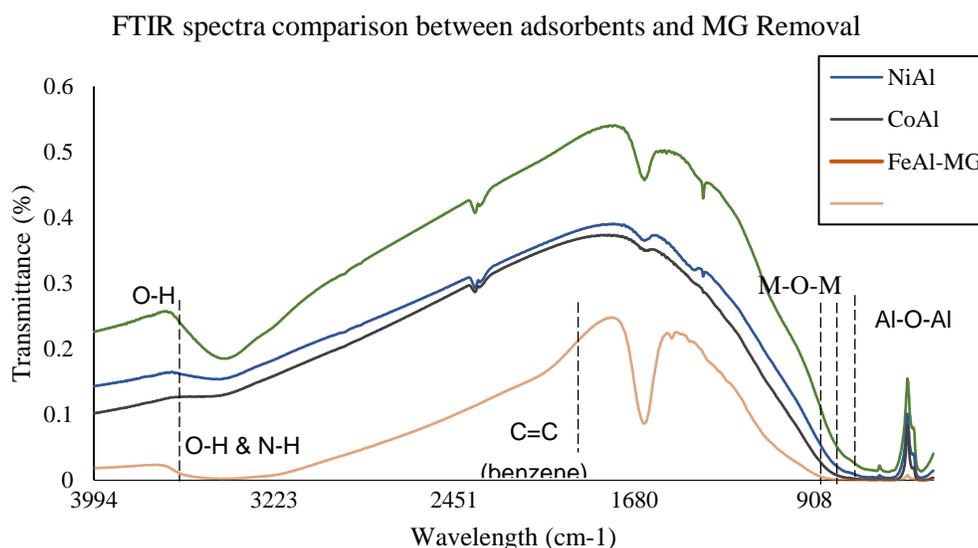


Figure 2: FTIR spectra of adsorbents; FeAl, CoAl, NiAl and after MG removal by FeAl

3.2 Adsorption of Malachite Green

A comparative study was performed to assess the removal percentage of MG by CoAl, FeAl and NiAl, involving contact time as the influence parameter. The batch adsorption study was conducted at nine different contact times (15, 30, 60, 75, 90, 120, 150, 180, 210 minutes) by taking an initial concentration of 25 mg L⁻¹ of MG onto the adsorbents (1.0 g each). Figure 2 shows the effect of contact time on MG adsorption.

3.3 Effect of Contact Time

The effects of contact time on MG adsorption by CoAl, FeAl and NiAl were studied over different time periods. CoAl was shown to be the most potential adsorbent for MG adsorption compared to FeAl and NiAl, as shown in Figure 2. Almost complete removal, with 94–97% removal of MG was achieved at 60 minutes onwards.

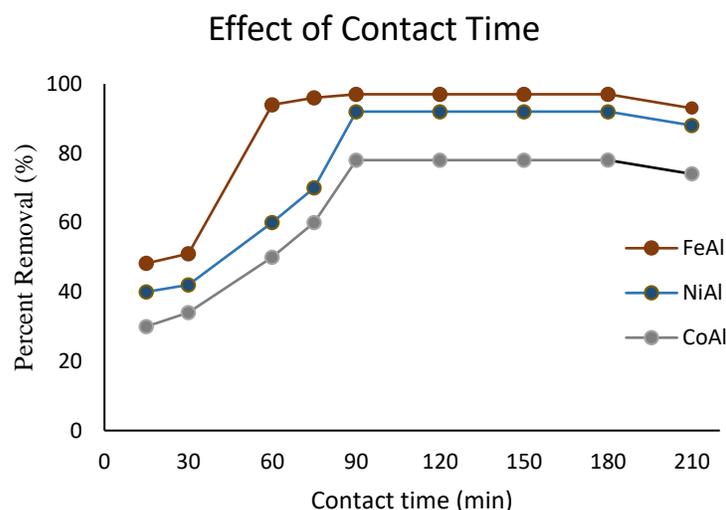


Figure 3. Effect of contact time on percent removal of 25 mg L⁻¹ of MG using CoAl, FeAl and NiAl.

As illustrated in Figure 3, the percent removal of MG using all adsorbents (CoAl, FeAl and NiAl) increased with increasing contact time until reaching equilibrium. All adsorbents showed significant role to remove MG in aqueous solution. The adsorption of all adsorbents showing significant increase from 30 minutes and kept increasing until reaching the equilibrium. A slight decrease was shown after reaching equilibrium.

FeAl removed around 94 - 97% MG from 60 to 180 minutes and reached equilibrium at 120 minutes. The percentage of adsorption remains unchanged after 120 minutes at 97% but slightly decrease to 93% at 210 minutes. A similar trend was observed from the adsorption of MG using NiAl and CoAl. Maximum removal of MG was observed at 90 minutes until reaching equilibrium at 150 minutes for both NiAl and CoAl with removal percentage of 92% and 78% respectively.

The absorption was rapid initially within the first 90 minutes due to the large available vacant site of the adsorbent as shown in Figure 2. A slowing trend was then observed later due to the depletion of remaining surface sites and repulsive forces between the adsorbed MG molecules. After 90 minutes, the interaction between the adsorbed MG molecules and the approaching MG molecules intensifies until all available sites are occupied. As time passed, exhaustion of the adsorbent's active sites occurred, thus achieving equilibrium at 120 minutes. Thus, 120 minutes was selected as the optimal contact time for the removal of 25 mg L⁻¹ MG by FeAl [14]. With the highest percent removal of 97% MG in aqueous solution by FeAl, the composite was concluded as the best potential

adsorbent among NiAl and CoAl, similar to the FTIR characterization with the intensity of the hydroxyl group of FeAl being the highest among NiAl and CoAl.

4.0 CONCLUSION AND RECOMMENDATION

This study was conducted to determine the ability of coated alumina adsorbent with different magnetism compounds of Co, Fe and Ni to remove MG in an aqueous solution. The chemical characterization of the adsorbent was conducted using KBR-FTIR revealed the presence of hydroxyl group, alumina and metal stretching in the structure, proving the coating of magnetism compound on the alumina. The presence of hydroxyl group on the composites showed that the adsorbents have a great affinity for dyes and act as an active site for the removal of the MG in aqueous solutions. The intensity of hydroxyl group can be the indicator of choosing the potential adsorbent as FeAl shows the highest intensity of hydroxyl group compared to the other two composites: CoAl and NiAl.

The ability of CoAl, FeAl and NiAl to adsorb MG was conducted with a variation of contact time. All composites showed a significant removal of MG, indicating the effectiveness of magnetism loading onto Al. The removal of MG using FeAl of about 97% was revealed at 120 minutes, followed by CoAl and NiAl with removal percentage of 92% and 78% respectively at 150 minutes. FeAl was selected as the best composite among CoAl and NiAl for further adsorption parameters. Further characterization, kinetic and related studies can be performed with further optimization parameter such as dosage of the adsorbent, pH, concentration, and temperature of the MG solution.

REFERENCES

- [1] Azhar, S. S., Liew, A. G., Suhardy, D., Hafiz, K. F., & Hatim, M. I. (2005). Dye Removal from Aqueous Solution by using Adsorption on Treated Sugarcane Bagasse. *American Journal of Applied Sciences*, 2(11), 1499–1503
- [2] Sartape, A. S., Mandhare, A. M., Jadhav, V. V., Raut, P. D., Anuse, M. A., & Kolekar, S. S. (2017). Removal of malachite green dye from aqueous solution with adsorption technique using *Limonia acidissima* (wood apple) shell as low cost adsorbent. *Arabian Journal of Chemistry*, 10, S3229–S3238. <https://doi.org/10.1016/j.arabjc.2013.12.019>
- [3] Srivastava, S., Sinha, R., & Roy, D. (2004). Toxicological effects of malachite green. *Aquatic Toxicology*, 66(3), 319–329. <https://doi.org/10.1016/j.aquatox.2003.09.008>
- [4] Hussien Hamad, M. T. M. (2023). Optimization study of the adsorption of malachite green removal by MgO nanocomposite, nano-bentonite and fungal immobilization on active carbon using response surface methodology and kinetic study. *Environmental Sciences Europe*, 35(1). <https://doi.org/10.1186/s12302-023-00728-1>
- [5] Maiti, P., Siddiqi, H., Kumari, U., Chatterjee, A., & Meikap, B. (2023). Adsorptive remediation of azo dye contaminated wastewater by ZnCl₂ modified bio-adsorbent: Batch study and life cycle assessment. *Powder Technology*, 415, 118153. <https://doi.org/10.1016/j.powtec.2022.118153>
- [6] Asim, T., Mamoona, Tahir, A., Nisar, N., Ali, A., & Sheikh, A. (2018). Alumina as environmentally stable adsorbent for the removal of dyesul black dye from wastewater. *Water Practice and Technology*, 14(1), 62–70. <https://doi.org/10.2166/wpt.2018.110>
- [7] Zhang, Y., Huang, S., Mei, B., Tian, X., Jia, L., & Sun, N. (2023). Magnetite/ β -cyclodextrin/fly ash composite as an effective and recyclable adsorbent for uranium (VI) capture from wastewater. *Chemosphere*, 331, 138750. <https://doi.org/10.1016/j.chemosphere.2023.138750>
- [8] Shittu OK, Stephen DI, Kure AH. Functionalization of biosynthesized gold nanoparticle from aqueous leaf extract of *Catharanthus roseus* for antibacterial studies. *African J Biomed Res* 2017;20(2):195–202. <https://doi.org/10.4314/AJBR.V20I2>

- [9] Wu CY, Tu KJ, Deng JP, Lo YS, Wu CH. Markedly enhanced surface hydroxyl groups of TiO₂ nanoparticles with superior water-dispersibility for photocatalysis. *Materials (Basel)* 2017;10(5):566. <https://doi:10.3390/ma10050566>
- [10] Allwar A, Sari MK, Rahmawati F, Amatullah AN. Synthesis and characterization of composite of Al₂O₃/activated carbon by hydrothermal method. *Key Eng Mater* 2019;801:298–303. <https://doi:10.4028/www.scientific.net/KEM.801.298>.
- [11] Junaid M, Khan MA, Hashmi ZM, Nasar G, Kattan NA, Laref A. Structural, spectral, magnetic and dielectric properties of Bi substituted Li-Co spinel ferrites. *J Mol Struct* 2020;1221:128859. <https://doi:10.1016/j.molstruc.2020.128859>
- [12] Pang T, Yang X, Yuan C, Elzatahry AA, Alghamdi A, He X, Cheng X, Deng Y. Recent advance in synthesis and application of heteroatom zeolites. *Chinese Chem Lett* 2021;32(1):328–338. <https://doi:10.1016/j.ccllet.2020.04.018>
- [13] Cheriaa, J., Khaireddine, M., Rouabhia, M., & Bakhrouf, A. (2012). Removal of Triphenylmethane Dyes by Bacterial Consortium. *The Scientific World Journal*, 2012, 1–9. <https://doi.org/10.1100/2012/512454>
- [14] Kumari, R., Khan, M. A., Mahto, M., Qaiyum, M. A., Mohanta, J., Dey, B., & Dey, S. (2020). Dewaxed Honeycomb as an Economic and Sustainable Scavenger for Malachite Green from Water. *ACS Omega*, 5(31), 19548–19556. <https://doi.org/10.1021/acsomega.0c02011>