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SYNTHESIS OF MICROCRYSTALLINE CELLULOSE (MCC)-FE_3O_4 FOR MALACHITE GREEN ADSORPTION; KINETICS, ISOTHERMS, THERMODYNAMICS, AND REGENERATION STUDIES

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Abstract

Synthesis, characterization, and adsorption study of MCC-Fe_3O_4 composite have been conducted as an adsorbent for Malachite green dye. Preparation of MCC-Fe_3O_4 was performed by mixing the precursor Fe^{2+} and Fe^{3+} with MCC in a basic solution. MCC-Fe_3O_4 was characterized using Fourier Transform Infra-Red (FT-IR) and X-Ray Diffraction (XRD). Adsorption studies were carried out by determining the kinetics, isotherms, thermodynamics, and adsorbent regeneration. The results showed that MCC-Fe_3O_4 was successfully synthesized with magnetic property and was able to adsorb malachite green dye with adsorption capacity of 3,52 mg/g and an adsorption efficiency of 96,75% using 0.04 grams of MCC-Fe_3O_4 at a contact time of 5 minutes and a temperature of 45 °C. Based on the adsorption data, the malachite green dye adsorption process using the MCC-Fe_3O_4 adsorbent followed a pseudo-second-order kinetics model, Langmuir isotherm, and could be used up to three regeneration process.

Keywords: Adsorption, Fe_3O_4, Malachite Green (MG), Microcrystalline cellulose (MCC).

1. Introduction

One of the dye used in the textile industry is Malachite Green (MG) ($C_{23}H_{26}N_2OCl$), a triphenylmethane type cationic colour substance [1] in the form of dark green crystalline solids [2]. Malachite green is widely used because it is cheap, easy to obtain, and the resulting colour effect is more attractive [3]. In addition, malachite green is widely used as a biocide in the field of aquaculture and is also used in several fields such as in the food industry as a dye [4]. However, the build-up of Malachite green can interfere with the immune system and reproductive system of living things, as well as being carcinogenic and genotoxic [3].

Several methods have been used in the treatment of dye waste such as membrane filtration, electrochemical degradation, bioremediation, biodegradation, coagulation or flocculation, chemical precipitation, chemical oxidation, ozonation, and photocatalysis [5]. However, this method is less effective because it requires high operational costs.

Adsorption is an efficient colour substance processing technique and relies on high surface area and porosity [1]. Adsorption is considered one of the best methods because it has high efficiency, greater flexibility, simple design, ease of operation, and low cost [5].

Cellulose is widely used because it has a surface that is easy to chemically modify that can encourage the increase in the adsorption capacity of dye in water [6]. At the same time, magnetite (Fe_3O_4) is one of the iron oxide compounds that have strong magnetic properties so that many are modified with other materials [7]. Fe_3O_4 has several advantages including cheap, abundant, non-toxic [8] and has good magnetic properties and shows good adsorption capacity for the removal of heavy metals and dye in solution [9, 10]. However, Fe_3O_4 magnetite tends to fragment significantly due to the magnetic dipole interactions that occur. Therefore, to reduce deficiency, Fe_3O_4 is modified using activated carbon, silicon, silane, cyclodextrin, nanocellulose, and other compounds. It aims to produce a homogeneous distribution of nanoparticles and produce diverse activity [11].

In this research, the synthesis of MCC-Fe_3O_4 composite was conducted to be used as an adsorbent for malachite green dye, in which this adsorption study is still limited. Modification of MCC with magnetite aimed to reduce Fe_3O_4 fragmentation, adding active groups for adsorption, while at the same time producing MCC-based adsorbents that have high magnetic properties, so that it could be separated using external magnetic fields after the adsorption process [7].

2. Material and methods

2.1. Instrumentations

This research was conducted at Laboratory of Chemistry Department, Universitas Islam Indonesia. Instrumentations used in this study were Memmert electric oven, UV-Visible U-2010 spectrophotometer, FT-IR (Fourier Transform Infrared Spectroscopy) Thermo Nicolet Avatar 360, and X-Ray Diffraction (XRD) Bruker D2 Phaser 2nd Gen.

2.2. Materials

The materials used in the study were Microcrystalline Cellulose (MCC) (Avicel pH 101) NF,Ph.Eur., JP., iron (III) chloride hexa-hydrate ($FeCl_3{\cdot}6H_2O$) (Merck, Germany) PA, iron (II) chloride tetra hydrate ($FeCl_2 \cdot 4H_2O$) (Merck, Germany) PA ammonia (NH_3) 25% (Merck, Germany) ISO, Reag.PhEur., distilled water, plastic wrap, malachite green, weigh paper, and filter paper.

2.3. Methods

2.3.1. Synthesis of microcrystalline cellulose (MCC) with Fe_3O_4

MCC (15 g) is added with 1 mole (7.5 ml) of $FeCl_2 \cdot 4H_2O$ + 2 mole (7.5 ml) $FeCl_3$ $6H_2O$ and left for 30 minutes to absorb the ferrite solution. After 30 minutes added with a 25% NH3 solution to a pH of 10 while stirring at low speed for 20 minutes. The dissolved material is filtered and washed with distilled water until its pH becomes neutral. Furthermore, the modified MCC is dried in the oven for 3 hours at a temperature of 105 °C. The result is a black suspension of a mixture of MCC and magnetite.

2.3.2. Effect of adsorbent dose

The experiment was conducted by adding MCC-Fe_3O_4 of 0.01, 0.03 and 0.04 g to a 5-ppm malachite green solution of 20 mL stirred at a speed of 140 rpm for 30 minutes. It is further measured using UV-Vis at a wavelength of 617 nm.

2.3.3. Comparison of adsorption capacity

Comparison of malachite green adsorption capacity by Fe_3O_4, MCC, and MCC-Fe_3O_4 is done by mixing each adsorbent as much as 0.04 g with a 5 ppm malachite green solution of 20 mL and stirred at a speed of 140 rpm for 30 minutes.

2.3.4. Effect of pH

MCC-Fe_3O_4 with an optimal adsorbent dose of 0.04 g was added to 5 ppm malachite green as much as 20 mL at different pH (4, 6, and 8) by adding 0.1 M H_2SO_4 and 0.1 NaOH to adjust the pH. After that, the mixtures were shaken for 30 minutes at a speed of 140 rpm and were analyzed using a UV-Vis Spectrophotometer at a wavelength of 617 nm.

2.3.5. Adsorption kinetics

The adsorption kinetic study was conducted by adding 0.04 g of MCC-Fe_3O_4 to a 20 mL 5 ppm malachite green solution with different contact times (0. 5, 15, 30, 45, 60, 75, and 90) minutes at pH 8 stirred at a speed of 140 rpm. It is further measured using UV-Vis at a wavelength of 617 nm.

2.3.6. Adsorption isotherm

MCC-Fe_3O_4 with an optimal adsorbent dose of 0.04 g was added with malachite green with various concentrations (40 ppm, 50 ppm, 60 ppm, 80 ppm, 90 ppm, and 100 ppm) as much as 20 mL at optimum pH. After that, the mixtures were shaken for 30 minutes at a speed of 140 rpm and were analyzed using UV-Vis Spectrophotometer at a wavelength of 617 nm. The adsorption equilibrium data were analyzed using the Langmuir and Freundlich model.

2.3.7. Effect of temperature

Adsorption malachite green is done at 25 °C, 35 °C, and 45 °C. In this experiment, the concentration value of malachite green was 5 ppm, MCC-Fe_3O_4 was 0.04 g, and pH was maintained at pH 8. It is further measured using UV-Vis at a wavelength of 617 nm.

2.3.8. Regeneration

After being used to adsorb malachite green, MCCFe_3O_4 was dried in an oven at 105 °C to dry, then soaked in 10 mL of 0.1 M HCl solution for 30 minutes. Next, MCC-Fe_3O_4 was washed using distilled water until the pH was neutral to remove the remaining HCl and baked in an oven until the weight was constant. After that, re-adsorption of 20 mL of 5 ppm malachite green at an optimal pH of 8 using MCC-Fe_3O_4 at an optimal adsorbent dose of 0.04 g was carried out using a shaker for 30 minutes at a speed of 140 rpm and analyzed using Double Beam UV-Vis Spectrophotometer at a wavelength of 617 nm. These steps are repeated three times.

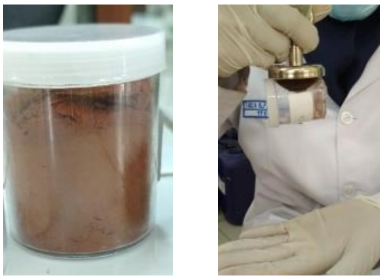
3. Results and Discussion

3.1. Synthesis of Microcrystalline Cellulose (MCC) with Fe_3O_4

Synthesis of Microcrystalline Cellulose (MCC) with Fe_3O_4 begins with reacting iron(II) chloride tetra hydrate ($FeCl_2 \cdot 4H_2O$) and iron (III) chloride hexahydrate ($FeCl_3$ $6H_2O$) with a mole ratio of 1:2. The reaction is as follows:

$$FeCl_{2(aq)} + 2FeCl_{3(aq)} + 8NH_4OH_{(aq)} \rightarrow Fe_3O_4 \downarrow_{(s)} + 8NH_4Cl_{(aq)} + 4H_2O_{(l)} \quad (1)$$

This suspension was added to MCC and set to basic, resulting a brownish black mixture. The dried modified composite was tested by applying a magnetic force that could observed in Fig. 1. In Fig. 1(b) MCC-Fe_3O_4 showed good magnetic properties that was seen from the interaction that occurs between MCC-Fe_3O_4 and magnets.



(a) (b)

Fig. 1. Dried MCC-Fe_3O_4 (a), Interaction between MCC-Fe_3O_4 and magnet (b).

3.2. Characterization of MCC, Fe_3O_4, and MCC-Fe_3O_4 using FT-IR

Characterization of compounds using FT-IR is performed to confirm synthesis results and compare function groups present in MCC, Fe_3O_4, and MCC-Fe_3O_4. The resulting FT-IR spectra display peaks that indicate the presence of a specific functional group in a typical wave number area. Based on the results of the analysis, obtained the spectra FT-IR Microcrystalline Cellulose (MCC), Fe_3O_4, and MCC-Fe_3O_4 as presented in Fig. 2.

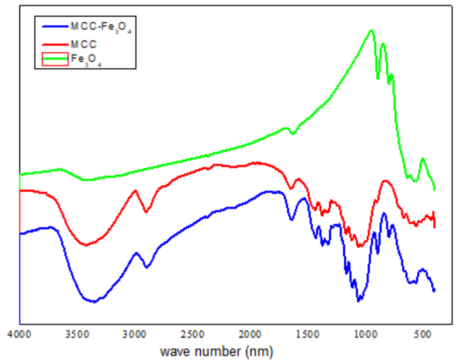


Fig. 2. IR spectra of microcrystalline cellulose (MCC), MCC-Fe_3O_4, and Fe_3O_4.

Based on Fig. 2., the function group information contained in each adsorbent in the form of a graph that illustrates the relationship between the percentage of transmittance (%T) and the wave number.

In the MCC spectrum (Fig. 2.), it was observed that there were O-H group (3420.92 cm^{-1}), C-H group (2900.13 cm^{-1}), C=O group (1645.35 cm^{-1}), C-O-C group (1432.70 cm^{-1}), C-O group (1373.69 cm^{-1}), -CH_2 group (1166.55 cm^{-1} and 1114.37 cm^{-1}), and C-H bending at 1058.15 cm^{-1}.

While in the MCC-Fe_3O_4 spectrum obtained information there is an absorption peak at wave numbers 612.98 cm^{-1} indicates the vibration of Fe-O bend in line the results of the Fe_3O_4 IR spectra that showed the absorption peak of 560.38 cm^{-1} indicates the presence of tetrahedral Fe-O group.

3.3. Characterization of Fe_3O_4 and MCC-Fe_3O_4 using XRD

Fe_3O_4 and MCC-Fe_3O_4 characterization uses XRD to determine the crystal structure and crystal size of the sample. Diffractograms for Fe_3O_4 and MCC-Fe_3O_4 are presented as in Fig. 3.

Based on the results of XRD characterization in Fig. 3 it can be known that Fe_3O_4 synthesis has a crystalline form. This is indicated by the high and sharp peak angle of XRD data which indicates the crystalline properties formed are also high. From the results of Fe_3O_4 characterization, obtained five peaks at an angle of 2θ consecutively of 35.9°; 36,0°; 35,6°; 30,6°; and 36,7°. The 2θ angles read on the Fe_3O_4 diffractogram indicate the data's conformity with JCPDS cards No. #19-0629 indicating that the main compound characterized is magnetite (Fe_3O_4). The crystalline properties of Fe_3O_4 are indicated by the appearance of diffraction peaks (311), (311), (311), (220), and (222). The crystal size obtained from the five main peaks was around 121 nm.

From the results of XRD characterization for MCC-Fe_3O_4, it is obtained the five highest peaks on the diffractogram at 2θ of 22.7°; 36,7°; 21,2°; 35,9°; and 34,7° with consecutive dipharaxial peaks (200), (222), (200), (311), and (311). After Fe_3O_4 was modified with Microcrystalline Cellulose (MCC), new diffraction peaks appeared such as peaks with an index (200) at angles of 2θ 22.735° and 21.239° indicating the peak of cellulose. From each of the 2θ known distance between grids

(d) consecutively which is 4.3370 Å; 2,7103 Å; 4,6393 Å; 2,662 Å; and 2.8636 Å, while the crystal size obtained was around 67 nm.

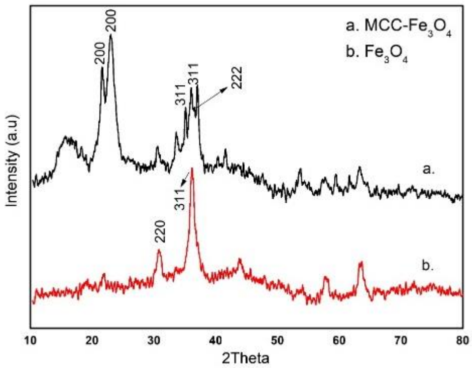


Fig. 3. Diffractogram of Fe_3O_4 and MCC- Fe_3O_4.

3.4. Effect of adsorbent dose

The effect of the dose of adsorbent is shown in Fig. 4. Based on Fig. 4. It is shown adsorption of malachite green dye is optimal at adsorbent doses of 0.04 g with adsorption percentage of 75.43%, while at adsorbent doses 0.03 g and 0.01 g adsorption percentage is 72.61% and 69.27%. It is known that there is an effect of adsorbent doses used with the adsorption ability of malachite green dye where the more doses of adsorbent used, the more active side on the surface of the adsorbent the greater the contact between adsorbent and adsorbates the greater and more dye are absorbed.

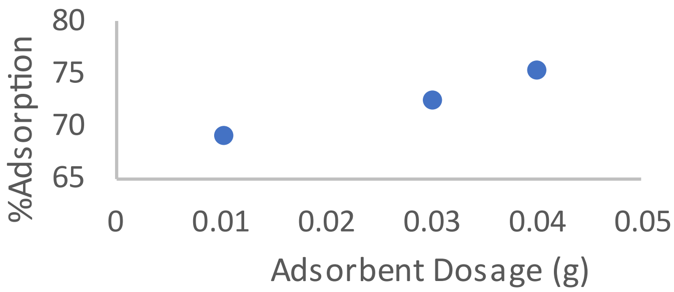


Fig. 4. Effect of adsorbent dosage on %adsorption.

The ability of Microcrystalline Cellulose (MCC)-Fe_3O_4 to absorb malachite green dye is affected by the interaction between Microcrystalline Cellulose (MCC)-Fe_3O_4 (Fig. 5) which is anionic with the cationic dye.

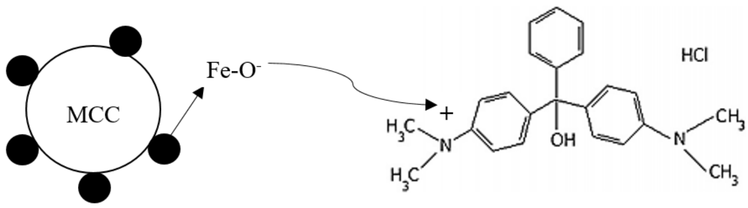


Fig. 5. Interaction between MCC-Fe_3O_4 and malachite green.

3.5. Comparison of adsorption capacity of adsorbent

Comparison of adsorption capacity of adsorbent is done to compare adsorption performance of each adsorbent namely MCC, Fe_3O_4, and MCC-Fe_3O_4.

Table 1. Adsorption capacity of each adsorbent.

Repetition	Adsorption Capacity (mg/g)		
	MCC	Fe_3O_4	MCC-Fe_3O_4
1.	1.6989	1.8667	1.8210
2.	2.1211	1.7955	1.8108
3.	1.7141	1.9430	1.8057

The data in Table 1 obtained is then analyzed using the one-way ANOVA single factor test. This test is used because the data variables are analyzed more than two and aims to determine the effect or difference in adsorbent variation on adsorption of malachite green. Based on the results of the single-factor ANOVA test, the P-value of 0.89 is greater than 0.05, so it can be concluded that there is no significant difference in the adsorption capacity of each adsorbent.

3.6. Effect of pH

Based on Table 2., these results show that pH 8 is the optimal pH that can be used to adsorb malachite green because it has the highest adsorption percentage than the others, which is 95.91%. The most influential factor on the effectiveness of the adsorption process, one of which is to use the suitable pH. Efficiency increases as the pH degree increases due to deprotonation on the surface of the adsorbent and causes the concentration of OH^- to increase through electrostatic interactions, so that hydrogen bonds in the adsorbent will adsorb malachite green molecules or cause precipitation of malachite green so that it can be separated from the filtrate and combine with the adsorbent. is at the bottom of the bottle. Meanwhile, if the pH value is smaller or acidic, the efficiency will decrease because it can cause the concentration of H^+ to increase and cause the adsorption of hydrogen ions to the adsorbate surface to become positively charged, resulting in a strong repulsion between the cationic dye molecules (green malachite) and the adsorbent surface.

Table 2. Adsorption of malachite green onto MCC-Fe_3O_4 in various pH.

pH	qe (mg/g)	%Adsorption
4	1.72	65.84
6	2.48	95.32
8	2.50	95.91

3.7. Effect of temperature

Adsorption of malachite green dye at a temperature of 25 °C (298.15 K) can absorb malachite green dye as much as 3.4461 mg/g with absorption efficiency of 90.2581%, While at a temperature of 35 °C (308.15 K) malachite green dye can be absorbed as much as 3.4588 mg/g with an absorption efficiency of 90.5912%, and at a temperature of 45 °C (318.15 K) can absorb malachite green dye as much as 3.5224 mg/g with absorption efficiency of 92.2565%.

From the results of the study, it is known that there is a temperature influence on the adsorption ability of malachite green dye where adsorption at high temperatures can increase adsorbent absorption to adsorbate because adsorbent pores are more open when heating occurs so that the interaction between adsorbent and adsorbates becomes stronger and can increase the absorption efficiency of malachite green dye.

The thermodynamic parameters specified are Gibb's energy (ΔG°), enthalpy change (ΔH°), and change in entropy (ΔS°). Gibb's energy (ΔG°) is calculated using the formula:

$$\Delta G° = -RT \ln K$$

Gibbs energy (ΔG°) is obtained at a temperature of 298.2; 308,2; and 318.2 with the K value of -4353.5; -4597,8; and -5310.8 J/mol, respectively. The three temperature variations show Gibbs energy (ΔG°) which is negative and decreases as the temperature increases. This suggests that the adsorption process is spontaneous, and the adsorption process is more optimal at higher temperatures.

Determination of the values ΔH° and ΔS° is done by plotting a graph of 1/T vs ln K from the equation:

$$\ln K = -\frac{\Delta H°}{RT} + \frac{\Delta S°}{R}$$

Graph 1/T vs. ln K can be seen in Fig. 6. The values ΔH° and ΔS° are determined by the slope and intercept values in the graph of the relationship 1/T vs ln K, which are -11183.6 kJ/mol and +5.6966 kJ/mol.K, respectively. The enthalpy change (ΔH°) obtained is negative which indicates that adsorption takes place exothermically, while the positive value of the change in entropy (ΔS°) indicates that there is no significant structural change.

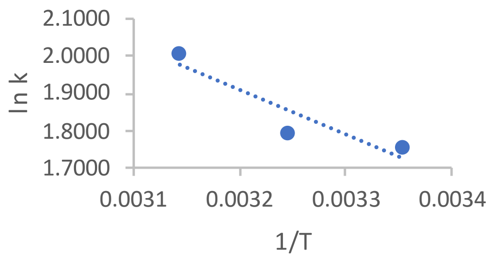


Fig. 6. Relation of 1/T vs ln k.

3.8. Effect of contact time and kinetics of adsorption process

Determination of contact time is done to find out the time it takes adsorbent to absorb dye when reaching equilibrium in the adsorption process of malachite green dye using MCC-Fe_3O_4. In this study, the variation in contact time was 0, 5, 15, 30, 45, 60, 75, and 90 minutes.

The results of an analysis of the effect of MCC-Fe_3O_4 contact time on malachite green dye can be seen in Fig. 7.

Based on the results in Fig. 7., the optimal contact time MCC-Fe_3O_4 to absorb the colour substance malachite green is 5 minutes. At that time, there is an equilibrium in the adsorption process where MCC-Fe_3O_4 absorbs malachite green dye optimally. In this optimum condition, there is an increase in the percentage of adsorption reaching the maximum point so that the addition of contact time does not have a significant influence on the absorption of malachite green dye.

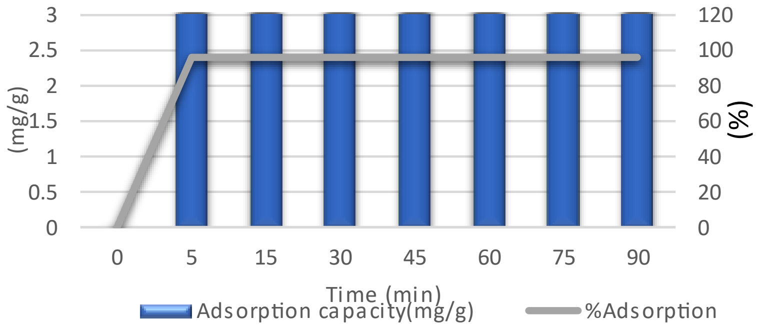


Fig. 7. The effect of contact time on adsorption capacity and percentage of adsorption of malachite green dye.

In the 15th minute there is a decrease in the percentage of adsorption and adsorption capacity due to the desorption process, which is the process of releasing adsorbate from the surface of the adsorbent. The decrease in adsorption rate towards the end of the experiment showed monolayer formation on the adsorbent surface caused by reduced active sites needed to absorb further malachite green dye after reaching equilibrium.

In adsorption kinetics are used two kinetic models, namely the pseudo-order one and the pseudo-two order to determine the kinetics of adsorption. The data obtained is put into the two kinetic models to produce a graph. From the graph, it can be determined the reaction rate constant (k), the equilibrium value of adsorption at the time t (qt), and the correlation coefficient value (R^2) of each adsorption kinetic model that can be seen in Table 3.

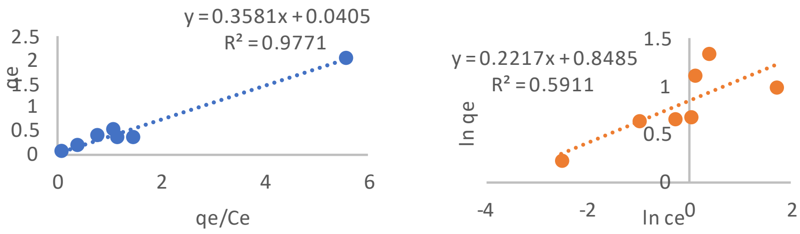
Table 3. Malachite green dyes adsorption kinetics by MCC-Fe_3O_4 using pseudo-first order and pseudo-second order.

Pseudo first order			Pseudo second order			qt experiment (mg/g)
$k_{1\ ads}$ (menit^{-1})	qt (mg/g)	R^2	$k_{2\ ads}$ (menit^{-1})	qt (mg/g)	R^2	
-0.0401	0.1785	0.3852	-4.2857	2.9343	1	2.9552

The adsorption capacity at the time of t(qt) of the color substance malachite green by the MCC-Fe_3O_4 pseudo-order model is 2.93 mg/g. This value is closer to the adsorption capacity at the time of t (qt) of the experimental result of 2.95 mg/g when compared to the adsorption capacity at the time of t (qt) of the pseudo-order model. The value of the correlation coefficient (R2) obtained is 1. From the results of adsorption kinetics, it can be concluded that the adsorption of malachite green dye by MCC-Fe_3O_4 follows a pseudo-two-order adsorption kinetic model that shows that chemical adsorption is dominant and controls the mechanism in the adsorption process.

3.9. Adsorption isotherm

Adsorption isotherm is used to determine the type of adsorption that occurs. Determination of the type of adsorption in terms of the magnitude of the linear regression value generated by the graph of each isotherm. By comparing the regression values of Langmuir and Freundlich isotherms in Fig. 8., the adsorption of malachite green by MCC-Fe_3O_4 follows the Langmuir isotherm theory with a regression value of 0.9732 and was a chemisorption. Langmuir's isotherm theory assumes that the monolayer of the adsorbate will be on top of the homogeneous adsorbent monolayer and adsorption will occur in certain homogeneous areas of the adsorbent



(a) (b)

Fig. 8. (a)Langmuir isotherm graph and (b) Freundlich isotherm graph.

3.10. Regeneration

Reusable adsorbent is an important point of the efficiency of making an adsorbent for waste. Besides not needing to re-synthesize to make new adsorbents in a long time and in a difficult way, this can also minimize space because it does not require a lot of space, is economical, and practical. In this analysis, HCl was used to regenerate MCC-Fe_3O_4 which had been used to adsorb malachite green previously, the result from 3 cycles regeneration data was shown in Fig. 9. A single factor ANOVA test was also carried out on the adsorption capacity data from the regeneration process with a p value of less than 0.05 and it can be concluded that there are significant differences in adsorption capacity from one regeneration process to another.

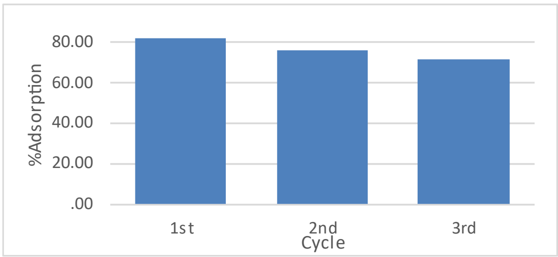


Fig. 9. Adsorption percentage from three cycles regeneration.

4. Conclusions

Based on the research that has been done, it can be concluded that the results of Fe_3O_4 modified MCC characterization using Fourier Transform Infra-Red (FT-IR) and X-Ray Diffraction (XRD) showed that MCC-Fe_3O_4 was successfully synthesized and showed good magnetic properties judging by the interactions that occur between MCC-Fe_3O_4 and magnets. MCC-Fe_3O_4 can optimally absorb malachite green dye of 3.5224 mg/g with absorption efficiency of 96.75% using 0.04 g of MCC-Fe_3O_4 at contact time for 5 minutes and temperature of 45 °C. The adsorption capacity of the composite was not significantly different with the MCC and Fe_3O_4. Adsorption kinetic model obtained in the adsorption of malachite green dye using the MCC-Fe_3O_4 adsorbent follows the pseudo second-order kinetic model, namely the adsorption velocity occurs due to the absorption at a solid phase with the mechanism of absorption on the surface of the adsorbent with a coefficient relation value (R^2) of 1 with the adsorption isotherm followed Langmuir model. Meanwhile the adsorbent could be reused up to three cycles of adsorption.

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