Application of modified green algae *Nannochloropsis* sp. as adsorbent in the sequential adsorption of methylene blue and Cu(II) cations in solution

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Abstract

Biomass of algae is a very potent adsorbent for absorbing liquid waste containing heavy metals and organic dyes. This study purposes to confirm the ability of adsorbents from green algae *Nannochloropsis* sp. modified with silica (ASN) and followed by coating magnetite particles (ASN-MPs) to absorb simultaneously the mixture of methylene blue (ME) and Cu(II) cations in aqueous solution. Simultaneous sorption of ME and Cu(II) cations to ASN and ASN-MPs was carried out by the Batch method with the interaction pH condition 7, contact time (15-120 minutes), and initial concentrations of ME and Cu(II) cations (0.1 - 1.0 mmol·L⁻¹). The simultaneous sorption parameters of ME and Cu(II) cations by ASN-MPs trend to comply the pseudo-second-order kinetics model by rate constant values for pseudo-second-order 

\(k_2\), respectively 8.98 x 10⁻³ and 9.78 x 10⁻³ (g·mmol⁻¹·min⁻¹). The ME adsorption pattern and Cu(II) cations in the competition on ASN-MPs adsorbents, each tends to follow the Freundlich and Langmuir adsorption isotherms. Based on adsorption data, Cu(II) cations have a greater adsorption rate and capacity \(q_{exp}\) compared to ME at the same contact time and initial concentration. Modified adsorbent from algae *Nannochloropsis* sp. with silica matrix and magnetite particle coating, is an adsorbent
that has a high effectiveness in the collective sorption of ME and Cu(II) cations. Therefore, these adsorbents can be used for the adsorption of cation mixtures of heavy metals and organic dyes that are cationic in solution.

**Keywords:** Nannochloropsis sp; algae-silica-magnetite hybrid; adsorption; methylene blue, heavy metal, Cu(II) cation.

1. **Introduction**

Organic dyes and heavy metals are sources of pollutants that are often found in the environment, especially in waters. Heavy metals and dyes are produced from by-products or various industrial wastes such as textiles and petrochemicals. Heavy metals such as Cu exposed to the environment can come from electroplating plants, mining, industrial, and municipal wastes [1] while organic dyes such as methylene blue (ME) are applied considerably as agents of dyes in varied industry such as the pharmaceutical, leather, paper and textile industries [2]. Because of this, the presence of these toxic chemicals needs to be reduced from the environment so that they do not have a negative impact on human health and the surrounding environment.

At present, several methods have been developed to reduce pollution from liquid waste in the form of physicochemical technology including ion exchange, coagulation,
floculation, chemical oxidation, electrochemical techniques, membrane separation, adsorption, and photocatalysis which have been applied for the purpose of removing dyes and metal ions from waste water [3-11]. From some of these technologies, the adsorption method is more often used for the treatment of liquid waste containing heavy metals or hazardous dyes. This is done with the consideration that the process of adsorption method is really easy, the cost applied is not expensive, and it is safe for the environment [12-13]. Sorption processes typically use adsorbents derived from the synthesis or modified natural material.

Currently, various adsorbents have been developed from natural materials for waste treatment before being discharged into the environment, such as algal biomass. Biomass from algae is originally a very potent adsorbent to absorb pollutants of inorganic materials like heavy metals [14-16] and organic materials originated from toxic dye agents [17,18]. Adsorption of metal ions and dyes on algal biomass occurs through reaction mechanisms involving the contribution of active groups of proteins, polysaccharides, and functional groups like hydroxyl, amino, sulfate ions, carboxyl, etc. [11, 19, 20].
Algal biomass has a great potential to bind dyes, especially organic dyes in the form of cations as well as metal ions. Several studies have shown that live algae and its biomass may absorb organic cations and metal ions [21, 22]. To increase the capacity and rate of algal adsorption on adsorbents absorbed as well as physical and chemical stability, various attempts were made including modifying algal biomass using various supporting matrix in the form of inorganic and organic materials [2,19]. Materials produced from inorganic-organic hybrids, such as algal-silica hybrids, are very promising substances for poisonous dye and heavy metal ion adsorbents [23-26].

The physical and chemical quality of adsorbents derived from algae were able to be performed by employing the sol-gel process in making adsorbents with silica support matrices, because these processes produce homogeneous adsorbents [27-30]. In addition, a rising in the sorption rate capacity of the adsorbate is able to be carried out using magnetite particle coating techniques [31-33]. The adsorbent coating technique by particles of magnetite is safe for environment, since it does not produce side products that conceive contamination like suspended solids, besides that it also accelerates the process of isolating the adsorbate from the solution caused by the magnetic properties of the adsorbent [34-38]. By using the adsorbent coating technique using magnetite
particles, we will get an adsorbent with a big adsorption rate and capacity to the adsorbate, so that the adsorption process becomes more efficient.

In a waste treatment system, multicomponent mixtures are often found, namely the presence of various types of chemical compounds both inorganic and organic compounds, therefore it is necessary to develop an adsorbent that is not only effective at absorbing heavy metals, but also effective against other compounds such as dyes contained in the mixture from ME. Therefore, the purpose of this work is to learn the competition for sorption of a mixture of ME and Cu(II) cations in solution on modified Nannochloropsis sp. (algae-silica-magnetite). The adsorbents used in this study have complex chemical and biological compositions, so it is very interesting to study from a theoretical and experimental point of view in their application as a material for absorbing dyes and metal ions in solution. Biomass from Nannochloropsis sp. algae has been modified with silica followed by coating with magnetite (Fe₃O₄) particles utilized as an effective and cheaper adsorbent to separate ME and Cu(II) cations simultaneously from the solution. The adsorption competition between ME and Cu(II) cations in ASN-MPs adsorbents was studied with a series of batch experiments including: variations in contact time, initial concentration, sequential desorption, and
re-use of adsorbent tests. Simultaneous adsorption kinetics and isotherm parameters as well as their mechanism are confirmed to predict the sorption properties of ME and Cu(II) cations by ASN-MPs.

2. Materials and methods

2.1. Materials

The used materials in this work include *Nannochloropsis* sp. algae originating from Balai Besar Budidaya Laut Lampung (the Lampung Sea Cultivation Bureau), Republic of Indonesia. The used chemicals were obtained from European Pharmacopoeia consisting of: tetraethyl orthosilicate (TEOS), FeSO$_4$·4H$_2$O, FeCl$_3$·6H$_2$O, HCl, NaOH, ethanol, methylene blue (ME), CuSO$_4$·5H$_2$O, and Na$_2$EDTA.

Magnetite particles were synthesized according to the procedure by Buhani *et al* [14].

2.2. Preparation of adsorbent and materials: *Nannochloropsis* sp., ASN, and ASN-MPs

*Nannochloropsis* sp. algae were neutralized (up to neutral pH) by rinsing with water, then dried for 3 days. The algae biomass was then placed at 40 °C for 2-3 hours then crushed using a 100 mesh grinder. The *Nannochloropsis* sp. algae biomass was used to make ASN-MPs adsorbents in the following way: a total of 5.0 mL of TEOS and 2.5 mL of deionized water was mixed into a plastic bottle, then gained 0.1 g
magnetite. The mixture was stirred for 30 minutes using a magnetic stirrer. When stirring, the pH of the solution was made to be pH of 2 with the addition of 1 M HCl by dropwise. In another bottle, *Nannochloropsis* sp. biomass (0.4 g) and ethanol (5 mL) were mixed by a magnetic stirrer for 30 minutes. Then, the two solutions were mixed while stirring until the mixture turns into a gel. The formed gel was filtered with filter paper and allowed for 24 hours. The gel was afterward rinsed using deionized water and ethanol with a ratio of 60/40 to pH≈7. Furthermore, the gel was placed in the oven to be dried at 40 °C for 2-3 hours and crushed using a grinder until smooth with a size of 100 mesh.

2.3. Characterization of ASN and ASN-MPs adsorbent

The ASN adsorbents and ASN-MPs were investigated by Fourier-transform infrared spectroscopy (FTIR) to recognize specific functional groups contained (Shimadzu Prestige-21 IR, Japan). The adsorbent crystallinity level was analyzed by XRD (Shimadzu 6000, Japan). The distribution of particle size from material was also investigated by the particle size analyzer (Fritsch Analysette 22). Surface morphological analysis and element constituents were performed using Scanning Electron Microscopy with Energy Dispersive X-Ray (SEM-EDX) (Zeiss MA10,
2.4. Adsorption experiments

The experimental procedure to study the adsorption competition between ME and Cu(II) cations in the mixture was carried out under the following adsorption conditions: a dose of 0.1 g ASN-MPs adsorbent was used in a batch system controlled by a shaker (Stuart reciprocating shaker SSL2), the sorption process was held at 27 ºC, interaction pH was 7, and an adsorbate volume was 50 mL. Experiments for investigating adsorption kinetics were performed with various time from 15 to 120 minutes while experiments to study the adsorption isotherm by varying the initial concentrations of ME and Cu(II) cations from 0.1 to 1.0 mmol·L⁻¹, respectively. UV-Vis spectrophotometer (Agilent Cary 100, U.S.A) was performed to analyze the concentrations of ME adsorbed on the adsorbent at a maximum wavelength of 664 nm. The concentrations of Cu(II) cations adsorbed by the adsorbent were tested with atomic absorption spectrophotometer (AAS) (Perkins Elmer 3110, U.S.A).

The Equations (Eqs.1, 2, and 3) were used to determine an amount of adsorbed ME or Cu(II) cations per unit mass of adsorbent and the percentage of adsorbed ME or Cu(II) cations.
\[
q_e = \frac{(C_o - C_f)}{m} x V \\
q_i = \frac{(C_o - C_i)}{m} x V \\
R(\%) = \frac{(C_o - C_f)}{C_o} \times 100
\]

Concentrations (mg·L\(^{-1}\)) of ME or Cu(II) cation solution at initial state, equilibrium, and certain time of \(t\) were expressed as \(C_o\), \(C_e\), and \(C_t\), respectively. The mass of adsorbent (g), the volume of the solution (L), the amount of ME or Cu(II) cations adsorbed per unit mass (mmol·g\(^{-1}\)), and the percentage of the ME or Cu(II) cation adsorption are expressed by \(m\), \(V\), \(q\), and \(R\), respectively.

2.4. Sequential desorption

To find out the type of interaction between ASN-MPs adsorbents with ME or Cu(II) cations, a sequential desorption experiment was conducted as follows: 0.1 g of ASN-MPs adsorbents were added to each ME or Cu(II) cation at conditions (pH = 7, \(T = 27°C\), \(t = 90\) minutes, volume = 50 mL, and adsorbate concentration 0.1 mmol·L\(^{-1}\)). Adsorbates adsorbed on the AS-MPs adsorbent were sequentially released using several eluents such as aquades, HCl (0.1 M), and Na\(_2\)EDTA (0.1 M).
2.5. Reusability of adsorbent

The ability to reuse adsorbents was studied by performing the adsorption process singly at the optimum condition. The adsorbate adsorbed was eluted by an eluent of 0.1 M HCl (50 mL). Then, the distilled water was used to rinse the adsorbent to reach neutral pH. The adsorption-desorption process was repeated several times, up to % adsorption from ME or Cu(II) cations < 80%.

3. Results and discussion

3.1. Characterization of ASN and ASN-MPs adsorbent

To find out the success of the modification process of Nannochloropsis sp. Algae using silica matrix and magnetite particle coating, identification of the adsorbent functional groups was carried out using FTIR. In ASN adsorbents (Fig. 1b) and ASN-MPs (Fig.1c), there is a relatively similar IR absorption with the appearance of absorption bands at wave numbers around 794.8 - 784.3 cm\(^{-1}\) originating from Si-O-Si and 482.9 - 432.9 cm\(^{-1}\) of the Si-O stretching vibrations (siloxan groups) derived from silica as a matrix. The contribution of Nannochloropsis sp. algae to ASN and ASN-MPs is indicated by the appearance of absorption bands in the region of wave number 2931.80 cm\(^{-1}\) originating from C-H stretching vibration absorption from (-CH\(_2\))
aliphatic as shown in Fig. 1a. In addition, absorption bands were seen in wave numbers
3448.72-3442.72 cm\(^{-1}\) originating from hydroxyl groups (-OH) and 1658.78-1651.07 cm\(^{-1}\) (carbonyl groups). This shows that there has been a hybridization between
*Nannochloropsis* sp. and silica matrix. The presence of magnetite particles in ASN and
ASN-MPs could not be observed through FTIR spectrum. In addition, the absence of
absorption in the area of wave number 964.41 cm\(^{-1}\) indicating the stretching vibration
of silanol (Si-OH) on the ASN-MPs adsorbent (Fig. 1c) as shown in the ASN spectrum
(Fig. 1b) indicates that there has been an interaction between the silanol groups and the
magnetite particles. The presence of magnetite particles in ASN-MPs is strengthened
from the results of the EDX spectrum [14].

Fig. 2 displays the morphology of ASN (Fig. 2a) showing an agglomeration
originating from the amorphous silica matrix and *Nannochloropsis* sp., this is supported
by elemental constituent data from the analysis of EDX on ASN (Fig. 2c) consisting of
Si, O, C, and N. The ASN-MPs adsorbent (Fig. 2b) shows a more contrasting
morphology and the presence of granules with smaller size and in the form of
agglomerate. This is supported by elemental constituent data obtained in EDX spectra
(Fig. 2d) showing the existence of Fe elements of magnetite particles, in addition to
other elements (Si, O, C, and N) as found in ASN.

The presence of magnetite particles in the modified *Nannochloropsis* sp. algae can be observed by comparing the XRD pattern between ASN and ASN-MPs (Fig. 3). The presence of magnetite particles (Fe$_3$O$_4$) in ASN-MPs can be seen from the results of the analysis with XRD (Fig. 3b). The XRD diffraction pattern in ASN-MPs has the most intense appearance at 2θ = 35.60 which corresponds to the diffraction pattern of Fe$_3$O$_4$ particles [39] which does not appear in ASN (Fig. 3a). The XRD diffraction pattern in ASN-MPs has a broad 2θ and lower intensity compared to Fe$_3$O$_4$, due to the presence of amorphous silica matrix [40] and *Nannochloropsis* sp. which cause a decrease in the level of material crystallization.

Addition of magnetite particles to ASN (Fig. 4b) results in a decrease in mean and median of particle size in ASN-MPs (Fig. 4c). The mean and median of particle sizes in ASN are 1.55 and 1.65 μm and in ASN-MPs are 1.40 and 1.53 μm, respectively. This shows the decrease in particle size after coating with Fe$_3$O$_4$ particles. In Fig. 4, it can be observed that there is a decrease in volume (%) for large particle size diameters from 12.92 in ASN to 11.70% in AS-MPs and an increase in volume (%) in small particle size from 3.50 in ASN to 4.73% in AS-MPs. These data are in line with the
results of observations on the surface morphology of adsorbents with SEM, as previously discussed, that the presence of Fe$_3$O$_4$ particles in ASN-MPs produces material with a relatively smaller particle size [11].

The adsorbent surface charge plays a significant part in determining the optimal interaction between adsorbent and adsorbate, therefore the surface charge of the adsorbent needs to be known in studying the sorption process. The surface charge is determined by the zero point of charge (pH$_{PZC}$) which is specified as the point when the zeta potential value has value of zero. The positive surface charge is indicated by pH < pH$_{PZC}$, whereas the negative surface is shown by pH > pH$_{PZC}$ [41]. In current study, the pH$_{PZC}$ of ASN and ASN-MPs is around 7.3 and 7.4 respectively observed by the method of solid addition (Fig. 5). Based on the pH$_{PZC}$ values of the two adsorbents, while the interaction pH in the collective adsorption process from ME and Cu(II) cation solution was conditioned at pH 7.0. This is with consideration, when the pH of the solution is below pH$_{PZC}$, the adsorbent will be positively charged while the ME solution and Cu(II) cations under these conditions will also be positively charged, so there will be a repulsion between the positive charge of the adsorbent and the adsorbate [42]. At pH 7, the interaction between adsorbent and adsorbate can occur optimally due to at the
pH, the adsorbent surface charge tends to be neutral and will be negative while the ME and Cu(II) cations solution are positively charged. At pH > 7 adsorption will tend to decrease, because adsorbates such as a solution of ME and Cu (II) cations will undergo hydrolysis which results in a negatively charged species. The same thing happened to the adsorbent surface charge which tends to be negative because of pH > pHpzc [31, 43]. Thus in this condition, there will be a repulsion between the negative charge of the adsorbent and adsorbate.

3.2. Simultaneous adsorption kinetics of ME and Cu(II) cations

The impact of interaction time on simultaneous sorption between solution of ME and Cu(II) cations can be seen in Fig. 6 showing that the amount of ME and Cu(II) cations adsorbed on ASN-MPs tends to be greater than ASN. In addition, Fig. 6 shows that Cu(II) cations are more adsorbed than ME dyes in both ASN or ASN-MPs. This shows that Cu(II) cations dominate more adsorbed in ASN and ASN-MPs.

To better understand the adsorption competition performance of ME dyes and Cu(II) cations adsorbed simultaneously, the adsorption kinetics model was used. Pseudo-first-order (Eq. 4) and pseudo-second-order (Eq. 5) kinetics [44, 45] could be applied to analyze the adsorption characteristics of ME dyes and Cu(II) cations shown
in Table 1.

\[ q_t = q_e (1 - e^{-k_1 t}) \]  (4)

\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \]  (5)

where \( q_t \) and \( q_e \) (mmol g\(^{-1}\)) are total adsorbate (ME or Cu(II) cation) adsorption capacity at certain time of \( t \) (min) and equilibrium, serially. While \( k_1 \) (min\(^{-1}\)) and \( k_2 \) (g·mmol\(^{-1}\)·min\(^{-1}\)) express the first and second order rate constants, respectively.

Table 1 describes the values from \( R^2 \) (linear correlation coefficient) of the pseudo-first and -second-order kinetics models compared, then both ME and Cu(II) cations on ASN and ASN-MPs are more likely to take the pseudo-second-order kinetics pattern. If \( k_2 \) values from ME and Cu(II) cations compared will indicate that Cu(II) cations are more adsorbed on both ASN and ASN-MPs. The presence of Fe\(_3\)O\(_4\) particles increases the adsorption rate of ME or Cu(II) cations in ASN-MPs.

3.3 Adsorption mechanism

The significant section in the investigation of adsorption kinetics is the adsorption mechanism, because it will give an overview of reaction happened between adsorbate and adsorbent. In the process of the adsorption, the amount of adsorbed adsorbate is always expected to be more adsorbed and easily released again.
The mechanism of adsorption between ME and Cu(II) cations is really controlled by the surface characteristics of the adsorbent used [46,47]. The mechanism of adsorption to ME and Cu(II) cations on ASN-MPs was analyzed using the proposal of Weber and Morris (Eq. 5) about the intra-particle diffusion pattern (IPD) [48, 49]. The IPD pattern can be utilized to study the diffusion process of targets absorbed by adsorbents that can be used in simulating kinetics data [50].

\[ q_t = k_{id} t^{0.5} + C \]  

(5)

Where the rate constant of intra-particle diffusion is stated by \( k_{id} \) (mmol·g\(^{-1}\)·min\(^{-0.5}\)), and a constant describing resistance for mass transfer in the border layer is represented by \( C \) (mmol·g\(^{-1}\)). Through the slope and intercept of lines resulted from plots of \( q_t \) versus \( t^{0.5} \) will be produced \( k_{id} \) and \( C \) (Fig. 7) and displayed in Table 2.

Fig. 7 describes two linear parts occurred for all plots. This model indicates that involvement of the adsorption models is more than one model. The external mass transfer occurs at the first linear section in the adsorption period of 0–60 minutes. The diffusion of intraparticle is indicated at the second linear section in the adsorption period of 60-120 minutes. The origin (\( C \neq 0 \)) does not traversed by the second linear part, this shows that the rate and external mass transfer is not controlled only by the
intraparticle diffusion but also it occurs simultaneously [48]. Based on observations
in Fig. 7, there are two steps that represent the migration of ME and Cu(II) cations
through the solution into the adsorbent external surface and further directed diffusion
through the adsorbate target into the adsorbent active site respectively through the pore
cavity and the adsorbent active group, according to diffusion theory at adsorption
process. The mechanism of adsorption may be illustrated in two dissimilar means
namely an electrostatic adsorption and a diffusion. This is because of the porosity and
existence of negative charge in the functional groups of adsorbents [42]. This is
supported by determining the mechanism of adsorption of ME and Cu(II) cations
through sequential desorption using several eluents such as distilled water, HCl solution,
and Na$_2$EDTA to release ME and Cu(II) cations which have been adsorbed on ASN-
MPs through entrapment interactions, electrostatic interaction, and complex formation
(Fig. 8).

In Fig. 8 can be seen the results of sequential desorption of ME dye and Cu(II)
cations contained in ASN-MPs by using an aquades eluent, HCl (0.1 M), and continued
with Na$_2$EDTA (0.1 M). Fig. 8 indicates that the percentage of ME dye and Cu(II)
cations eluted using 0.1 M HCl is greater than elution using water and 0.1 M Na$_2$EDTA
solution. This indicates that both ME and Cu(II) solutions adsorbed on ASN-MPs tend to be dominated by electrostatic interactions. ME is an organic cation and Cu(II) cation is positively charged so that it can interact with ASN-MPs which has a negatively charged surface. ASN-MPs tend to be negatively charged because they have functional groups consisting of hydroxyl, carbonyl, and amines from *Nannochloropsis* sp.. Whereas siloxan and silanol groups are from silica matrix.

3.4. *Adsorption isotherm*

The simultaneous competition for adsorption of ME and Cu(II) cations with varying initial concentrations of ASN and ASN-MPs can be seen in Fig. 9. The results illustrate that the amount of adsorbate adsorbed goes up with rising initial concentration of adsorbate used. In fact, at the use of high initial concentrations, the amount of adsorbate adsorbed reaches a maximum. In other words, increasing the concentration does not increase the amount of adsorbate adsorbed. This is due to a decrease in the quantity of available active sites accompanied by increasing the concentration of the ME solution and the adsorbed Cu(II) cations. The sorption capacity raises caused by an enhancement in the initial concentration of ME dyes and Cu(II) cations as a booster to
increase the adsorption capacity because in this condition there are more adsorbates which occupy the active sites on the adsorbent surface [51].

Fig. 9 states that the \( q \) value for Cu(II) cations is greater than that of ME in both ASN and ASN-MPs at the same initial concentration. In addition, it can also be seen that the \( q \) value of ASN-MPs adsorbents is relatively higher for ME and Cu(II) cations than ASN adsorbent. Furthermore, to investigate the sorption parameters of ME dyes and Cu(II) cations which were adsorbed simultaneously on ASN and ASN-MPs, then Langmuir (Eq. 6) and Freundlich (Eq. 7) adsorption isotherm models were employed [52,53] to describe quantitatively the ME and Cu(II) cations adsorption isotherms (Table 3).

\[
q_e = q_m \frac{K_L C_e}{1 + K_L C_e} \quad \text{(6)}
\]

\[
q_e = K_F C_e^{1/n} \quad \text{(7)}
\]

where \( q_e \) and \( C_e \) represent the amount of adsorbed adsorbate per unit weight of adsorbent (mmol·g\(^{-1}\)) and unadsorbed adsorbate concentration in solution at equilibrium (mmol·L\(^{-1}\)), respectively. \( K_L \) and \( K_F \) are the Langmuir constant (L·mmol\(^{-1}\)) and Freundlich constant, serially. While \( n \) shows Freundlich exponent. The Freundlich exponent \( n \) values were between 1-10. The analysis results of the adsorption data
using Langmuir and Freundlich adsorption isotherm models can be seen in Fig. 10 and Table 3. Table 3 and Fig. 10 show that the $R^2$ indicates that the adsorption isotherm pattern of ME is more likely to attend the Freundlich adsorption isotherm. Adsorption of ME dyes on ASN and ASN-MPs goes on multiform faces of multilayer adsorbents via physical interactions [54]. Adsorption of Cu(II) cations trend to take the Langmuir adsorption isotherm showing that the interaction of Cu(II) cations to adsorbents is a chemical interaction. The Langmuir isotherm assumes that each site of active adsorption and adsorbate binding ability is equivalent and does not depend on the adjacent site being occupied or not. This assumption shows that adsorption occurs in the surface layer of the adsorbent monolayer, after distributing the adsorption energy evenly to the entire surface [55,56]. From the simultaneous adsorption isotherm pattern of ME and Cu(II) cations in ASN-MPs, it may be assumed that Cu(II) cations have a greater adsorption capacity (Table 3). This shows that the active groups in adsorbents derived from algal biomass (hydroxyl, carbonyl, and amines groups) and silica matrix (siloxan and silanol groups) as well as the magnetic properties of adsorbents can raise the quantity of
available active sites on the adsorbent [11]. The Cu(II) cations are more easily adsorbed by ASN-MPs because Cu(II) cations have a smaller size (hydrated cation size (1.96 Å)) compared to ME which is a molecule with a greater size.

3.5. Reuse of adsorbents

The study of the ability to reuse adsorbents is one of the important parameters that needs to be determined to investigate the effectiveness of repeated use of adsorbents applied in the process of adsorption.

In this work, reuse of ASN-MPs adsorbents was carried out through an adsorption-desorption process of 5 repetitions of ME and Cu(II) cations (Fig. 11). The sorption results of ME and Cu(II) cations were released using distilled water and continued with solution of HCl (0.1 M). The HCl was effective as eluent to release ME and Cu(II) cations from ASN-MPs which were adsorbed through the electrostatic interaction mechanism. This interaction occurs through proton substitution of ME as organic cations [58] and Cu(II) cations as hydrated cations in solution. The adsorption-desorption process was carried out repeatedly 3 times and apparently it did not reduce the percentage of ME and Cu(II) cations adsorbed significantly (Fig. 11). The percentage of ME and Cu(II) cations adsorbed began to decrease at the 4th adsorption
repetition, this was caused by the reduction of the adsorbent active sites due to the desorption process and adsorbent washing.

4. Conclusions

Adsorbent production from *Nannochloropsis* sp. algae biomass modified by silica matrix and magnetite particle coating has been successfully carried out. The application of ASN-MPs adsorbents on the simultaneous adsorption of solution pair of ME and Cu(II) cations with the batch method shows that Cu(II) cations are more adsorbed than ME in simultaneous adsorption which is dominated by electrostatic interaction mechanism. Simultaneous adsorption of ME and Cu(II) cations by ASN-MPs trends to attend the pseudo-second-order kinetics model and the ME follows the Freundlich adsorption isotherm, while Cu(II) cations lean to take the Langmuir adsorption isotherm model. ASN-MPs adsorbent is very effective in absorbing ME and Cu(II) cations in solution and it can be used up to 3 times the adsorption repetition without a significant reduction in adsorption capacity. Thus, this adsorbent can be applied for the absorption of cation mixtures of organic dyes and heavy metals that are cationic in solutions derived from industrial waste.
Declarations

Availability of data and materials

The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

Competing interests

The authors declare they have no competing interests.

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Authors’ contributions

The manuscript was mainly based on a draft written by Buhani and Suharso, and written through contributions of all authors. All authors read and approved the final manuscript.

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