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Adsorption isotherm of multicomponent solution of Cu(II) ions, crystal violet, and methylene blue on Silica-Magnetite *Porphyridium* sp. algae hybrid

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Abstract. Algae-silica hybrid (HA-S) from *Porphyridium* sp. has been modified by coating particles of magnetite (Fe_3O_4) via a sol-gel process using (TEOS) to produce silica-magnetite algae hybrid (HA-SM). The produced material HA-SM was applied as adsorbent for the multicomponent solution adsorption of Cu(II) ions, crystal violet (CV), and methylene blue (MB). Identification of functional groups was performed by infrared spectrometer (IR) indicating that in HA-SM there are an active organic groups derived from *Porphyridium* sp., while silanol and siloxane derived from silica matrix. In addition, the results of the analysis using Scanning Electron Microscopy with Energy Dispersive X-Ray (SEM-EDX) showed HA-SM has more heterogeneous surface morphology. The adsorption model of the multicomponent solutions of Cu(II) ions, CV, and MB by HA-S and HA-SM tend to follow the model of Freundlich adsorption isotherm.

Keywords: *Porphyridium sp.*, HA-SM, adsorption, Freundlich

1. Introduction

Water pollution caused by heavy metals and dyes tends to increase [1-3], especially those originating from wastewater resulting from industrial activities that have an impact on environmental pollution with amount of more than 7×10^5 tons heavy metals could not be degraded in environment [4]. In addition, it could be both harmful to a variety of living species and easily to be accumulated through the food chain which may eventually affect human beings, more stable and dangerous due to the formation of more complex chemical structure and difficult to degrade [5].

The most widely used dyestuffs are crystal violet (CV) and methylene blue (MB) due to their properties with good solubility. The CV and MB are a basic aniline dyes with molecular formula $C_{25}H_{30}N_3Cl$ and $C_{16}H_{18}C_1N_3S$. The CV and MB dyestuffs are reported to cause a bad effects on humans, animals, and microorganisms as well as increase the environmental pollution. In addition, the CV and MB dyestuffs are an aromatic compound with a complex structure and hard to degrade. One of the heavy metal resulted from industrial waswater is Cu metal. Cu metal is needed by human beings for Fe metabolism in hemoglobin, but in high concentration, it will be toxic and accumulated in the human body [6,7].

Therefore, it is important to control the discharge of CV and MB dyestuffs also Cu(II) ions into the wastewater before they are being released into the environment effectively with process the wastes

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containing the dyestuffs and heavy metals before their discharged into the environment. Dyes waste water treatment can be done using adsorption method because it is simple, relatively inexpensive, and does not generate byproducts that are harmful to the environment [8,9]. The success of the adsorption process is determined by the compatibility of the nature and type of the adsorbent used. The effective adsorbent for adsorption is the adsorbent which has a large rate and adsorption capacity, chemical stability, environmental friendly, and it can be used repeatedly. In general, filtration and centrifugation are used after adsorption process. They are time consuming. The blockage of filters and the loss of adsorbents may occur in filtration method. The use of magnetic separation method offers an alternative way to solve these problems [10].

Several studies have been reported on the preparation of adsorbent and their adsorption of dyestuffs solutions, which consisted material of Fe_3O_4 [1], γ-Fe_2O_3 [2], and nanocomposite mesoporous silica. In order to increase the adsorption capacity of the magnetic adsorbent, the magnetic adsorbent synthesis can be combined by adding an active group derived from algae biomass. Algae biomass is naturally an effective adsorbent for absorbing pollutants in both inorganic compounds such as heavy metals [11] and organic compounds derived from dyestuffs [4]. Several studies have shown that algae are alive and in the form of their biomass can adsorb chemical compounds, especially those containing cations such as metal ions and organic cations. The adsorption ability of algae biomass as an adsorbent can be increased by immobilizing algae biomass using various supporting polymers which are generally inorganic solids such as silica [12]. Enhancement of adsorption rate from adsorbate on the adsorbent was carried out using magnetite particle coating technique on silica as a biomass support matrix [13].

In this study, HA-SM have been synthesized through a sol-gel process using tetraethyl orthosilicate (TEOS) as the precursor and organic group of *Porphyridium* sp. algae biomass and coated with magnetite particle. The synthesis of this adsorbent has never been done by previous researchers. The study of the adsorption of HA-SM material on the multicomponent solutions of Cu(II) ions, CV, and MB discuss about the adsorption isotherm of the absorbent to the multicomponent solutions of Cu(II) ions, CV, and MB. The HA-SM material is effective as an adsorbent for the removal of the multicomponent solutions of Cu(II) ions, CV, and MB, especially for the water treatment process from dyestuffs and heavy metals contaminants.

2. Experimental methods

2.1. Materials

Porphyridium sp. biomass was obtained from the Lampung Sea Cultivation Bureau (Balai Besar Pengembangan Budidaya Laut Lampung, Indonesia). All chemicals used in the research were purchased from Merck Co., Inc. (Germany) and consisted of TEOS; distilled water; HCl 0.1 M; NH_4OH 1 M; NaOH 0.1 M; $FeSO_4{\cdot}4H_2O$; $FeCl_3{\cdot}6H_2O$; MB; CV; $CuSO_4{\cdot}5H_2O$; ethanol; KNO_3 1 M; CH_4N_2O 0.1 M; and Na_2EDTA 0.1 M. Fe_3O_4 particel used in this study were synthesized based on procedures performed by previous researchers [13].

2.2 Preparation of HA-SM adsorbent

The HA-SM synthesis was carried out by interacting 5 mL of TEOS, 2.5 mL of distilled water, and 0.1 g of magnetite particle in a plastic bottle by stirring for 30 min. During stirring, 1M solution of HCl up to pH $\approx$ 2 (solution A). In a different plastic bottle, 0.1 g *Porphyridium* sp. biomass was mixed with 5 mL of ethanol, and the mixture was stirred for 30 min (solution B). By stirring, solution A was mixed with solution B to obtain a gel. The gel produced was left for 24 h, cleaned by water and ethanol up to the pH of filtrate was near 7, and then dried in an oven at 40 ºC until its weight was constant. The dried material was ground and sieved through a sieve of 200 mesh. Synthesis of HA-S was carried out by a similar procedure applied to yield HA-SM, but without adding the magnetite particle [14].

2.3 Characterization of HA-S and HA-SM adsorbent

The synthesis resulted in a material HA-S and HA-SM that was characterized by an infrared (IR) spectrometer Prestige-21 Shimadzu, Japan to identify functional groups that existed in the material. The surface morphology and constituent elements were investigated by Scanning Electron Microscopy with Energy Dispersive X-Ray (SEM-EDX) (Zeiss MA10, Germany).

2.4. Batch adsorption experiment

Batch adsorption experiments were carried out to estimate the efficiency of HA-S and HA-SM for the removal of the multicomponent solutions of Cu(II) ions, CV, and MB from the artificially contaminated water. Stock solution of the multicomponent solutions of Cu(II) ions, CV, and MB of 1; 2.45; and 3.13 mmol L^{-1} respectively was prepared by dissolving accurately 1 g in 1 L of distilled water from which the solutions of desired concentrations were prepared by dilution. The adsorption process by batch method was carried out by interacting 25 mL of the multicomponent solutions of Cu(II) ions, CV, and MB with pH = 8, and then adsorbent stirred at 15 min contact time and 100 rpm speed to determine the influence of solution concentration variation.

Concentration of multicomponent solution of Cu(II) ions, CV, and MB before and after adsorption processes is specified using AAS (Atomic Absorption Spectrophotometer) and UV-Vis Spectrophotometer (Agilent Cary 100, U.S.A.) at a wavelength of 591 (CV) and 664 nm (MB). The concentration of the multicomponent solutions of Cu(II) ions, CV, and MB adsorbed per unit mass of adsorbent and the percentage of the multicomponent solutions of Cu(II) ions, CV, and MB adsorbed was determined using Eqs. (1)-(2).

$$qe = \frac{(Co - Ce)}{m} \times V \tag{1}$$

$$qt = \frac{(Co - Ct)}{m} \times V \tag{2}$$

Where C_o is concentration in the initial state, C_e is concentration at equilibrium, C_t is concentration at a certain time t of solution (mg L^{-1}), m is the mass of adsorbent (g), V is the volume of the solution (L), q is the number of solution adsorbed per unit mass (mg g^{-1}).

2.5. Adsorption mechanism

Determination of adsorption mechanism was done using sequential desorption method, on the multicomponent solutions of Cu(II) ions, CV, and MB. It was started with the adsorption process using 0.1 g HA-S and HA-SM adsorbent and added with 25 mL the multicomponent solutions of Cu(II) ions, CV, and MB in the optimum concentration with the contact time of 15 min at 100 rpm stirring speed. The resulted material from centrifugation process was washed by distilled water, KNO_3, CH_4N_2O, and Na_2EDTA solution of 25 mL respectively.

3. Results and discussion

3.1. Characterization of adsorbent

Synthesis of HA-S and HA-SM materials was performed through a sol-gel process using TEOS as a precursor and continued with coating by magnetite particle. Characterization of the materials of HA-S and HA-SM included identification of functional group, crystalline level, particle size distribution, surface morphology, and material composition. Identification of functional groups with IR spectroscopy has been performed to find out HA-S modifications that produce HA-SM containing magnetite particles (Figure 1). In Figure 1(a) it can be observed that the IR spectra of the

Porphyridium sp. algae biomass showed the presence of –OH group bound to C=O, amplified by the appearance of uptake in wavenumber 1651.07 cm^{-1} which is a typical uptake of C=O of a carboxylic acid. In the wavenumber 3749.62 cm^{-1} there is a primary N–H group. Uptake in wavenumber 2931.86 cm^{-1} indicates the presence of a C–H group of a carbon (aliphatic) chain CH_2 [12].

In Figure 1(b) which is the IR spectra of HA-S and Figure 1(c) of HA-SM gives the same relatively IR uptake value that is the presence of strong uptake peaks in wavenumber 3425.58 cm^{-1} indicated the presence of O-H vibration. Uptakes in the 1651.07 cm^{-1} area show the O-H vibration of bound water molecules while 1049.28 cm^{-1} is an asymmetry vibration of the siloxane group (Si–O–Si). The existence of C–H stretch vibration indicates the presence of an aliphatic group ($-CH_2$) in the wavenumber region 2931.8 cm^{-1}. The uptake at 856.39 cm^{-1} explains the presence of symmetrical stretch vibration of siloxane groups from Si–O and in absorption regions 432.05 cm^{-1} indicates the vibration of Si–O [21]. In IR spectra for HA-SM there is also a magnetite group indicated by wavenumber 570.93 cm^{-1} overlapping with Si-O-Si uptake band in wavenumber 432.05 cm^{-1} as well as there exists wavenumber 856.39 cm^{-1} derived from Si–O stretch vibration [12].

SEM images and energy dispersive X-ray spectroscopy (EDX) spectra from HA-S and HA-SM are shown in Figure 2. The results of surface morphology analysis with SEM show morphological differences on surface HA-SM compared with HA-S, due to the presence of the magnetite particles. The HA-SM looks surface morphology which is more heterogeneous and contrast, this occurs because of the presence of Fe element derived from magnetite particles, while in the HA-S more dominated silica matrix so it is more homogeneous [15]. While the data EDX (Table 1) can also be known that on the HA-SM, besides there are constituent elements derived from the silica matrix and *Porphyridium* sp. biomass, there are also other elements that come from magnetite (Fe and O) as shown in Figure 2(b) and Table 1.

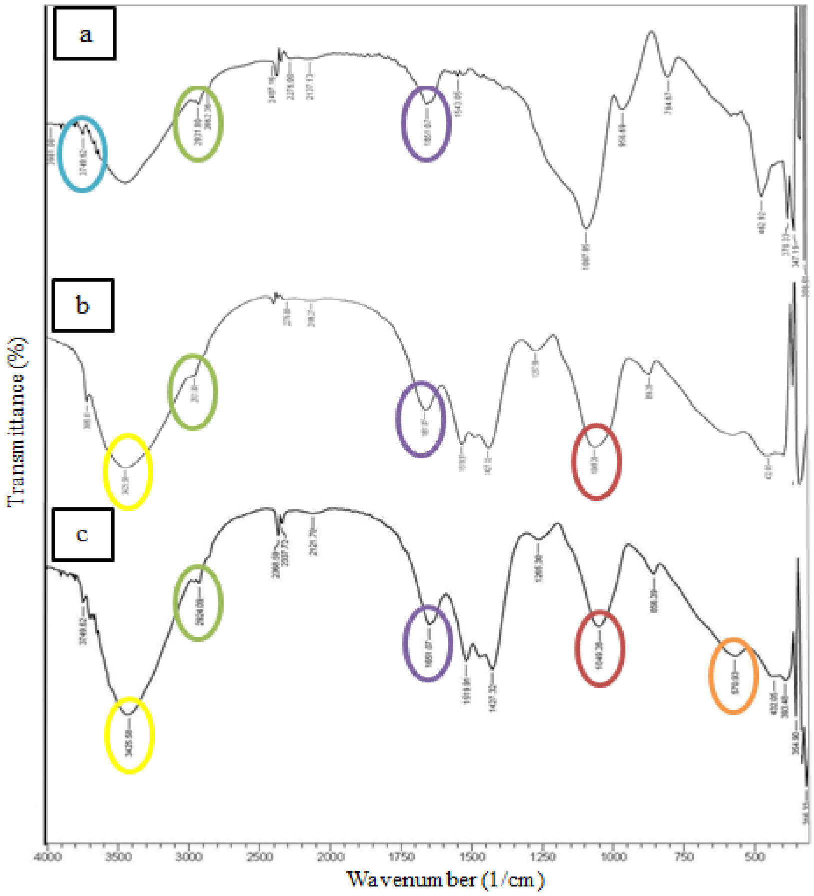

Figure 1. Infrared spectra of the (a) *Porphyridium* sp. (b) HA-S, and (c) HA-SM.

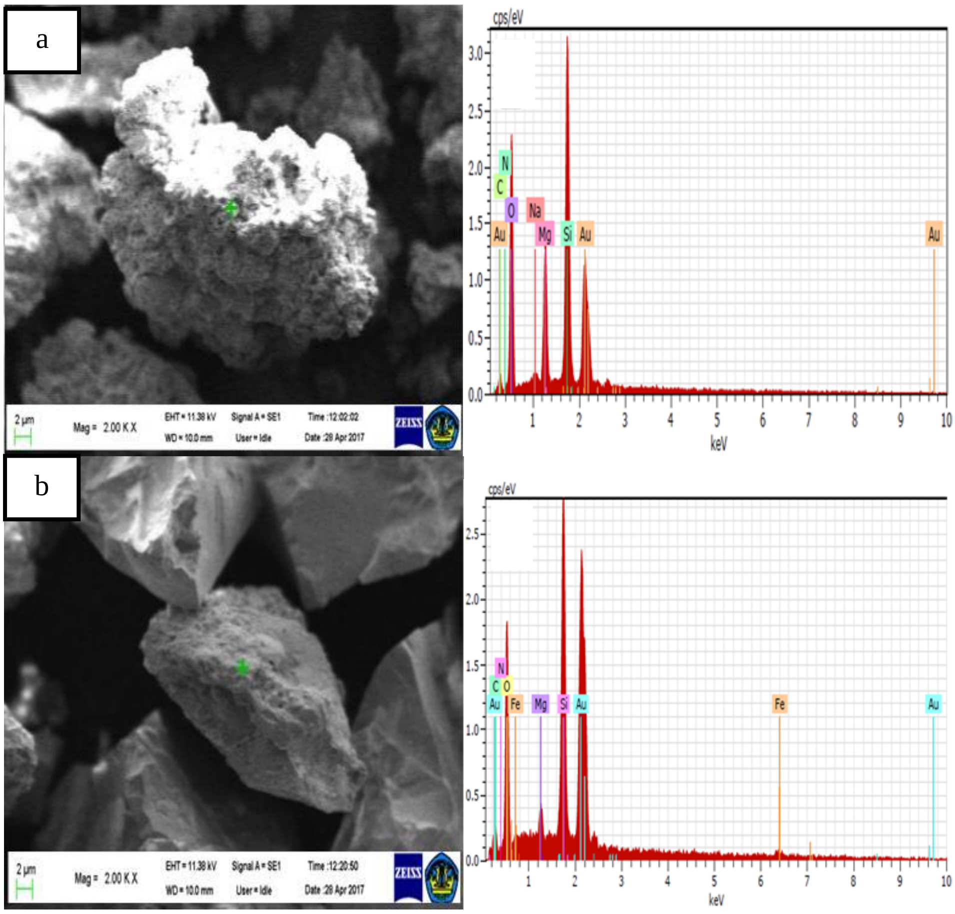

Figure 2. SEM images and EDX spectra of (a) HA-S and (b) HA-SM.

3.2. Adsorption

3.2.1. The influence of multicomponent solution of Cu(II) ions, CV, and MB concentration

The HA-S and HA-SM adsorption capability in absorbing the multicomponent solution Cu(II) ions, CV, and MB were investigated through the interaction of solutions at varying concentrations ranging from 0.1– 0.5 mmol L^{-1}. In Figure 3, it can be observed that there is an increase in the number of multicomponent solution Cu(II) ions, CV, and MB adsorbed with increasing concentration of solution. Adsorption of multicomponent solution of Cu(II) ions, CV, and MB increased sharply at low equilibrium concentrations and gradually increased at high concentrations. This shows that the HASM have a high adsorption affinity. In order to obtain the adsorption isotherm pattern that plays a role in describing the distribution between solution and solid phase, the data contained in Figure 3 were analyzed using adsorption isotherm models of Langmuir [Eq. (3)] and Freundlich [Eq. (4)] [8,14] as follows:

$$\frac{1}{q_e} = \frac{1}{q_m K_L C_e} + \frac{1}{q_m} \tag{3}$$

$$\log q_e = \log\ K_F + \frac{1}{n \log C_e} \tag{4}$$

Where C_e (mg L^{-1}) is the equilibrium concentration of solution, q_e (mg g^{-1}) is the adsorption capacity of solution at equilibrium, q_m (mg g^{-1}) is the adsorbent monolayer adsorption capacity, and K_L is the equilibrium constant including the affinity of binding sites (L mg^{-1}). K_L and q_m can be determined from the linear equation plot of log $1/q_e$ vs $1/C_e$ which will produce a straight line with $1/q_m K_L$ as slope and $1/q_m$ as intercept. K_F ((mg g^{-1}) (L $mg^{-1})^{1/n}$) is the adsorption capacity factor and n

is the adsorption intensity factor, with *n* values ranging from 1 to 10 [14]. Next, plot of log q_e vs log C_e will produce K_F and exponent of *n.* Langmuir adsorption isotherm model assumes that on the surface of the adsorbent, there are a certain number of active sites that are proportional to the surface area, the adsorbent surface is uniform, and the adsorption process is monolayer. While Freundlich adsorption isotherm model is an empirical equation employed for heterogeneous system and adsorption at multilayers [15,16]. The adsorption parameters of multicomponent solution Cu(II) ions, CV,and MB by HA-S and HA-SM shown in Table 1. Show that the R^2 value of the Freundlich adsorption isotherm model is higher than that of Langmuir, adsorption isotherm model for adsorption of multicomponent solution Cu(II) ions, CV, and MB both in HA-S and HA-SM [11,12].

This suggests that the adsorption model for multicomponent solution of Cu(II) ions, CV, and MB are more fitting to the Freundlich adsorption isotherm model supported by the adsorption of the experimental results closer to the Freundlich model (Figure 3). Similar results were reported for the adsorption isotherm of various organic pollutants onto activated carbon cloth. Freundlich constants (*n*) of multicomponent solution of Cu(II) ions, CV, and MB by HA-S and HA-SM (Table. 1) have values greater than 1. This indicates that the adsorption of multicomponent solution Cu(II) ions, CV, and MB on HA-S and HA-SM is favorable in this research. The multicomponent solution of Cu(II) ions, CV, and MB adsorption in HA-S and HA-SM not only occurs on active sites on the homogeneous (monolayer) adsorbent surface but also occurs reversibly on heterogeneous (multilayer) adsorbent surfaces. The presence of magnetite particle in HA-S causes adsorbent to be magnetite by increasing the removal rate of multicomponent solution of Cu(II) ions, CV, and MB from solution and the amount of multicomponent solution Cu(II) ions, CV, and MB adsorbed.

In addition, the presence of magnetite particle causes the particle size of HA-SM to be smaller than that of the HA-S. This increases the surface area on HA-SM so that the number of active sites will also increase [17]. Thus, it can be stated that the adsorption of multicomponent solution of Cu(II) ions, CV, and MB on HA-S and HA-SM not only occurs chemically through the interaction of anionic active groups with cationic multicomponent solution Cu(II) ions, CV, and MB but also occurs through the physical interaction due to the influence of the magnetite properties of the adsorbent.

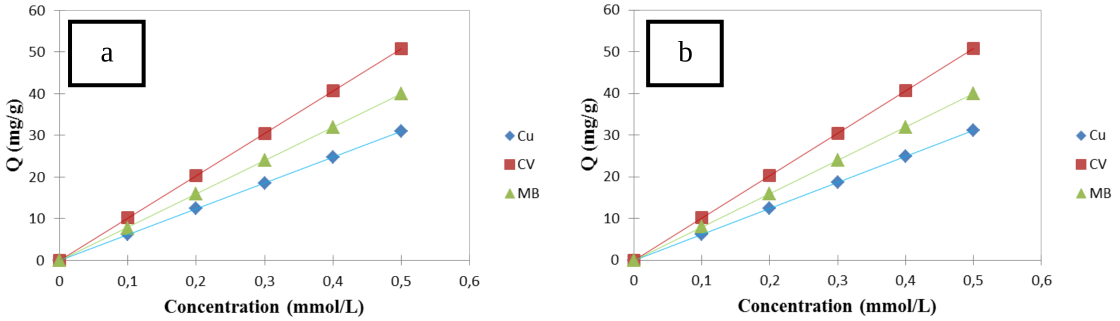

Figure 3. Influences of solutions concentration on adsorption multicomponent solution of Cu(II) ions, CV, and MB by (a) HA-S and (b) HA-SM (pH 8 and contact time 15 min).

Table 1. Langmuir and Freundlich parameters for the adsorption of multicomponent solution Cu(II) ions, CV, and MB on HA-S and HA-SM.

Adsorbent		**Isotherm Model**					
		Langmuir			**Freundlich**		
		n_m (mg/g)	**K_L (L/mg)**	**R^2**	**n**	**K_F (mg/g) (L/mg)$^{1/n}$)**	**R^2**
HA-S	**Cu(II)**	32.894	0.573	0.756	0.672	38.832	0.982
	CV	105.263	0.730	0.492	1.397	44.565	0.911
	MB	243.902	0.317	0.006	0.884	108.292	0.651
HA-SM	**Cu(II)**	227.272	0.366	0.026	0.970	96.360	0.907
	CV	121.951	0.650	0.972	1.267	49.808	0.993
	MB	52.356	6.586	0.530	1.655	79.341	0.859

3.2.2. Types of interactions

The occurred adsorption mechanisms show type of interactions in HA-S and HA-SM adsorbents to multicomponent solutions of Cu(II), CV, and MB was dominated by complex formation interactions (Figure 4.). The desorption percentage of Na_2EDTA eluent on HA-S adsorbents is 69.29; 85.63; and 67.43%, while on HA-SM is 62.89; 52.41; and 71.71% for Cu(II), CV, and MB respectively. The complex formation interaction between HA-S and HA-SM with the multicomponent solutions of Cu(II) ions, CV, and MB is caused by multicomponent solutions formed on the HA-S and HA-SM adsorbent surfaces due to the ionic process [12].

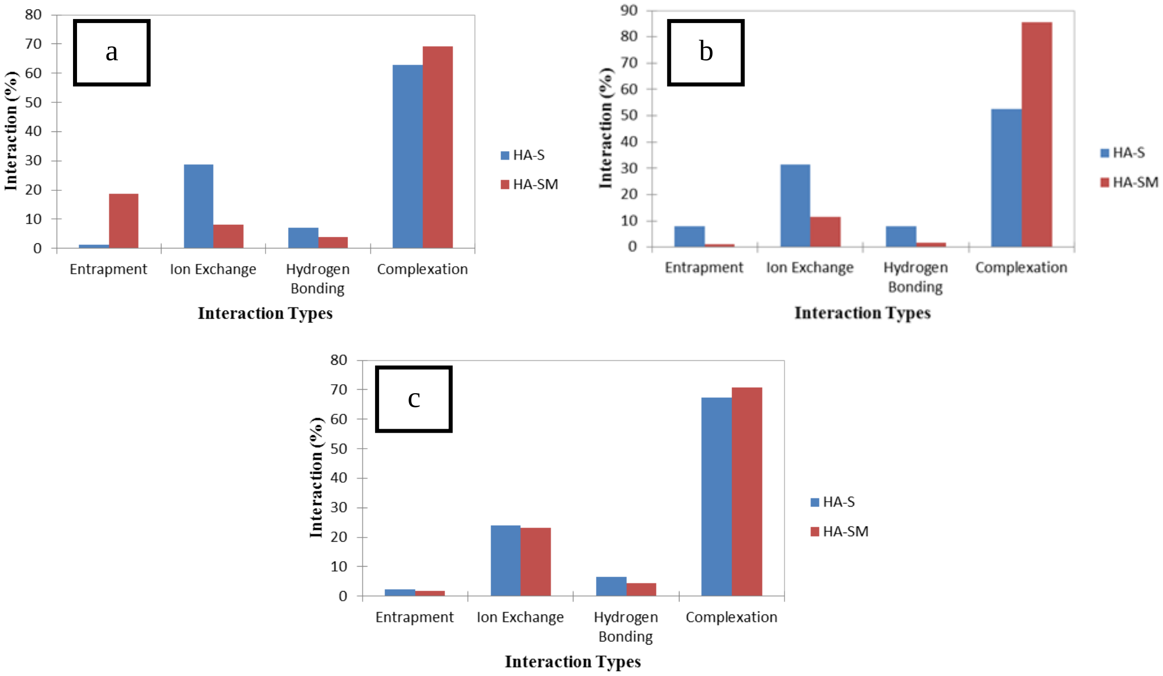

Figure 4. Types interaction HA-S and HA-SM the multicomponent solutions of (a) Cu(II) ions, (b) CV, and (c) MB.

4. Conclusions

Modification of HA-S derived from *Porphyridium* sp. algae biomass with the coating magnetite particle has produced an effective adsorbent to remove Cu(II) ions, CV, and MB in solution. Characterization of HA-SM material shows some active groups acting as active sites for binding of Cu(II) ions, CV, and MB. Coating magnetite particle increases the rate and capacity of the HA-S adsorption to the multicomponent solutions of Cu(II) ions, CV, and MB. In the HA-SM Materials, it is also proven that there are more complex bond interactions. Thus, HA-SM is an effective adsorbent for removing Cu(II) ions, CV, and MB in solution, so it can be applied to the processing of wastewater containing dyestuffs and heavy metals.

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