



Modification of *Chaetoceros* sp. Biomass with Silica-Magnetite Coating and Adsorption Studies towards Cu(II) Ions in Single and Binary System

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Adsorbent synthesis from *Chaetoceros* sp. biomass with silica-magnetite coating technique (ASMC) and without magnetite (ASC) has been performed through the sol-gel process. Both adsorbents were characterized by infrared spectrophotometer, X-Ray diffraction and scanning electron microscopy. The adsorption process of Cu(II) ions was performed in a single and binary systems using batch method. The adsorption data of Cu(II) ions on ASC and ASMC within a single system follows the pseudo kinetic model of order 2 with the adsorption rate of Cu(II) ions on ASMC faster than ASC. The adsorption isotherm model of Cu(II) ions on ASC and ASMC tend to follow Langmuir adsorption isotherm model with adsorption capacity of 57.77 and 105.91 mg g⁻¹, respectively. The ASMC material is not selective for Cu(II) ions with the ion pairs such as Ni(II), Zn(II), Cd(II) and Pb(II) ions.

Keywords: Adsorption capacity, *Chaetoceros* sp., Silica-magnetite coating, Heavy metals.

INTRODUCTION

Currently, efforts are processing waste containing heavy metals before being discharged into the environment is likely to increase. One of these efforts is with utilizing of natural materials such as biomass derived from algae, fungi and agricultural waste as heavy metal adsorbent [1,2].

Algal biomass is a natural material that has the ability to absorb heavy metals and has a considerable abundance in the waters. Utilization of algae as heavy metal adsorbent is still not optimal, whereas algae has great capability to bind heavy metals which are one source of environmental pollution. Some studies [3-5] have shown that the algae alive or in the form of biomass can effectively absorb heavy metals. But algae's ability to bind heavy metals is very limited by several problems such as small size, low specific weight and easily damaged due to degradation by other microorganisms [6,7]. In addition, algae cannot be used directly in the adsorption column, because it is very soft and no granular form [8]. To overcome these weaknesses, various attempts were made among others with immobilizing of algae biomass using a variety of support polymers.

Immobilization of algal biomass with a supporting matrix of silica has been done and managed to increase the adsorption capacity of the metal ions [9,10]. Enhancement of adsorption selectivity through an ionic imprinting technique on *Nannochloropsis* sp. biomass has also been performed [11]. Although

the material has been obtained modified algae biomass is the best properties, such as high capacity, large adsorption selectivity, and chemically stable. In use as an adsorbent, the material causes problems due to suspended solids formed (flocclulants) that inhibit the process of separating metals from solution, consequently the adsorption process is slower and produces by-products in the form of suspended solids that are less environmentally friendly [12,13].

Improving the quality of adsorbent can be done by applying a sol-gel process in the synthesis of algal biomass with a supporting matrix such as silica, because the process can produce homogeneous adsorbent [14,15]. Increasing the adsorption rate of metal ions on the adsorbent can be performed using coating technique of magnetite (Fe₃O₄) particle on silica as a supporting matrix of biomass [16,17]. Silica coating technique with magnetite particles are techniques that are environmentally friendly, because it does not form a product containing contaminants such as suspended solids, besides accelerating the process of separation of metals from solutions for magnetic adsorbent [18,19]. By using this technique, it will obtain the adsorbent which has a large capacity and selectivity towards target metal ions and can separate target metals quickly [13].

The primary objective of this study is to study the adsorption capacity of the material synthesized algae biomass *Chaetoceros* sp. (brown algae) by coating silica-magnetite, Cu(II) ions in the singular and the competition with metal ions such as Ni(II),

Zn(II), Cd(II) and Pb(II) ion as a pair ion (binary system) in the solution.

EXPERIMENTAL

Synthesis ASC and ASMC: Synthesis of ASMC was done by mixing 5 mL of TEOS and distilled water into a plastic container, then added 0.1 g Fe_3O_4 [16], with constant stirring for 30 min. When stirring, 0.1 M HCl was added dropwise until pH of the solution reached 2 (solution A). In another container, 0.4 g *Chaetoceros* sp. biomass blended with ethanol, and then stirred for 30 min (solution B). Subsequently solution A was mixed with solution B with stirring to form a gel. The gel was formed and then allowed to stand for 24 h. The gel was washed using distilled water and ethanol until the filtrate becomes pH 7. Then the gel was dried in an oven at 40 °C to constant weight. The dried material was crushed to 200 mesh size. Synthesis of ASC was performed in the same way as ASMC procedure but without the addition of Fe_3O_4 .

The materials produced were characterized by IR Prestige-21 Shimadzu for identification of functional groups. Obtained crystals were analyzed by XRD (Shimadzu 6000). The surface morphology of material was analyzed by SEM (JSM 6360 LA). Metal ion concentrations were determined using atomic absorption spectrophotometer (AAS) Model Perkins Elmer 3110.

Single system adsorption: The adsorption process was performed to determine, optimum pH, contact time and adsorption isotherm model. Determination of adsorption pH was determined with interacting 50 mg of adsorbent with 20 mL of Cu(II) ion (concentration of 100 mg L^{-1}) at varying pH of 2-8, the solution was added with buffer $\text{CH}_3\text{COONa}/\text{HCl}$ (pH 3) and $\text{CH}_3\text{COONa}/\text{CH}_3\text{COOH}$ (pH 4-6). The influence of contact time was made by reacting 50 mg of adsorbent in a series of test tube and supplemented with 100 mg L^{-1} of each Ni(II) ion solution at pH optimum with the interaction time varied 0-90 min.

The adsorption isotherms of Cu(II) ions were studied with interacting 50 mg of adsorbent placed into a series of test tube, then added with a solution of each Cu(II) ions with varying concentrations of 0-500 mg L^{-1} . The adsorption was done in a batch system using a magnetic stirrer at temperature of 27 °C, optimum pH and time.

The amount of metal adsorbed per unit mass of adsorbent was calculated as follows:

$$q = v(C_o - C_t)/m \quad (1)$$

where C_o and C_t (mg L^{-1}) is a metal ion concentration before and after the adsorption process, m is the amount of adsorbent (g) and v is the volume of solution (L).

Binary system adsorption: The amount of 50 mg of adsorbent interacted with 20 mL of solution containing ion pairs Cu(II)/Ni(II), Cu(II)/Zn(II), Cu(II)/Cd(II), and Cu(II)/Pb(II), with each concentration of 0.5 mmol L^{-1} . The adsorption was performed in a batch system using a magnetic stirrer at pH 6 for 60 min.

RESULTS AND DISCUSSION

The ASMC synthesis was performed through sol-gel process by TEOS hydrolysis followed by mixing magnetite and the addition of algae biomass *Chaetoceros* sp. in ethanol.

Infrared spectra (Fig. 1c and 1d) show the adsorption patterns which are relatively similar to the silica absorption spectra (Fig. 1b). The addition of new absorption existed in the wave number 2924.09 cm^{-1} derived from C-H stretching vibration adsorption of (- CH_2) aliphatic shows that hybridization occurred between silica and algae biomass *Chaetoceros* sp. has been successfully performed in ASC and ASMC. Disappearing of the band at 964.41 cm^{-1} which is stretching vibration (Si-O) on ASC and ASMC showed that the completion of the condensation process [10,11].

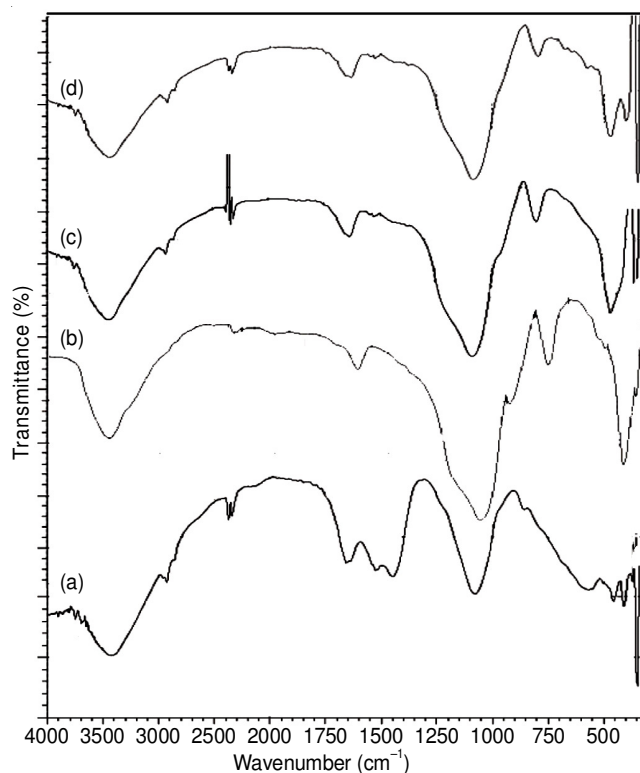


Fig. 1. IR spectra of (a) *Chaetoceros* sp. algae, (b) silica, (c) ASC and (d) ASMC.

Analysis of the crystal structure of the synthesized material was performed using XRD. Peaks that are contained in the diffractogram then be identified using methods search match methods with file data standard contained in the file PCPDFWIN program 1997 [20,21]. From the analysis, it is known that the diffraction peaks of ASMC (Fig. 2b) are different from the ASC (Fig. 2a). It is also observed that the diffractogram of ASMC has 2θ as existed on the diffraction peak structure of typical of crystalline Fe_3O_4 , namely: 35.468; 62.602; 30.133; 57.02021 (Fig. 2b). Based on the analysis, it can be stated that ASC has the structure of a basic form (amorphous) while ASMC indicates magnetite crystals formed (crystoballite).

The analysis results of the surface morphology with SEM (Fig. 3) show the difference between ASC surface morphology (Fig. 3a) and ASMC (Fig. 3b). The surface morphology ASMC looks more contrast than the surface morphology ASC because of the existence of Fe_3O_4 particles in the material. The existence Fe_3O_4 leads to higher accelerating because it contains high atomic number, resulting in a wide scattering that produces a higher intensity so much contrast.

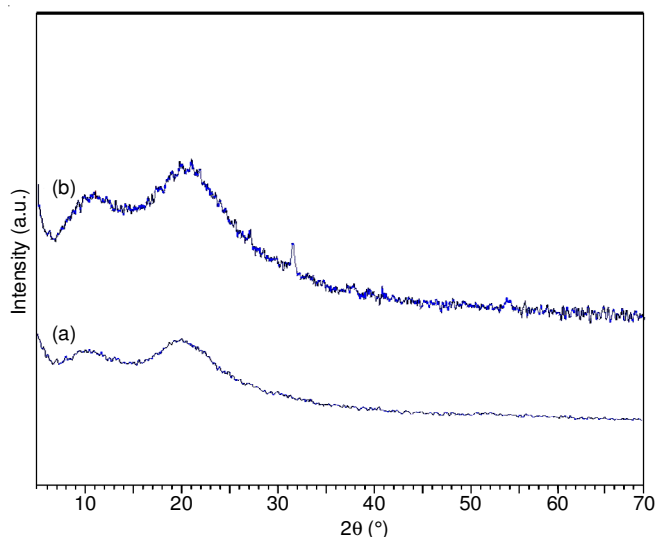


Fig. 2. Typical XRD patterns of (a) ASC and (b) ASMC

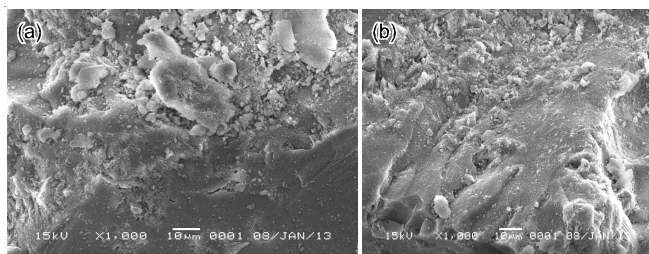


Fig. 3. SEM of (a) ASC and (b) ASMC

Effect of pH: Interaction of Cu(II) ions with ASC and ASMC was studied in the pH range of 2-8. Effect of pH on Cu(II) ions in solution with ASC and ASMC (Fig. 4) showed that the adsorption of Cu(II) ions was optimum at pH 6 with the percentage of Cu(II) ions adsorbed on ASC and ASMC by 80 and 97 %, respectively. At low pH, the adsorption process is not optimal because the active groups contained in ASC and ASMC occurred protonation resulted in the binding of H⁺ and H₃O⁺. This will reduce the availability of active groups on the adsorbent to form a complex with metals in solution [10,11].

At pH 6, the adsorption process tends to optimum. This is due to the active sites on ASC and ASMC are in the neutral

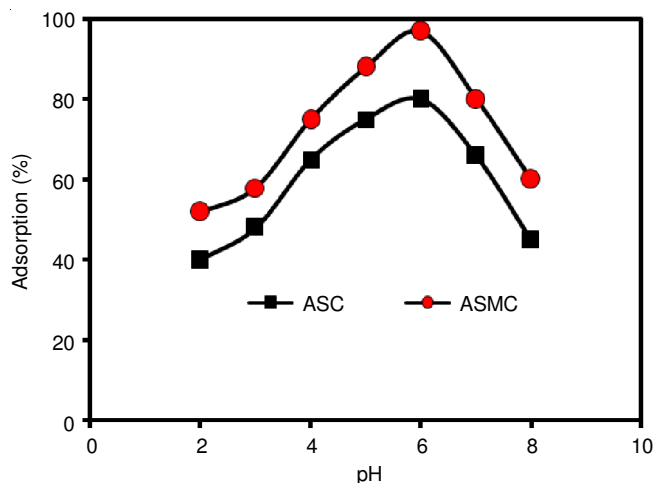


Fig. 4. Percentage adsorption of Cu(II) ion on ASC and ASMC material at pH interval of 2-8 (conc. 100 mg L⁻¹ and temp. 27 °C)

form as an amino, hydroxyl and carboxyl group derived from algal biomass [22-24]. Thus, these functional groups can serve as electron-pair donor and produces a strong interaction with metal ions of Cu(II). In addition, on ASC and ASMC still contained -OH (silanol) and -Si-O-Si- (siloxane) which can also act as a donor in these conditions, because it tends to negatively charged. At pH 6, the adsorption begins to decline, since Cu(II) ions started hydrolyzed to form deposited metal hydroxide species [25,26].

Adsorption kinetics: Effect of interaction time of Cu(II) ion on ASC and ASMC is presented in Fig. 5. From Fig. 5, it can be seen that in general the adsorption of Cu(II) ion takes place relatively quickly. In first 15 min, the adsorption increased very sharply, after 15 min, there was a slight increase in Cu(II) ion adsorbed and achieve constant at 60 min. At this stage, the adsorption process is estimated to reach equilibrium and extra time did not give rise to the amount of metal ions adsorbed significantly.

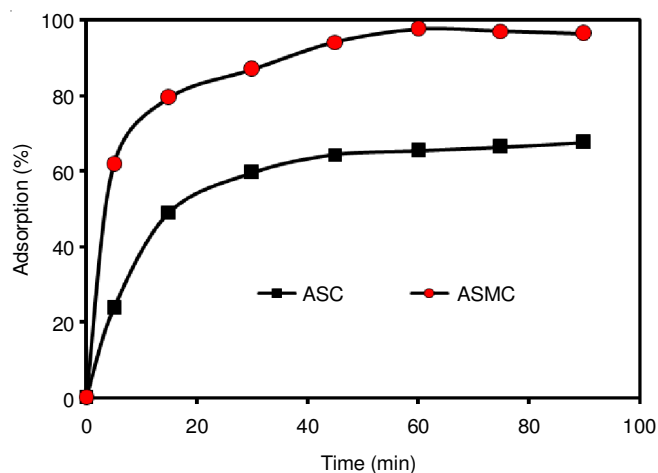


Fig. 5. Effect of interaction times versus amount of Cu(II) ion adsorbed on ASC and ASMC at pH 6 (conc. 100 mg L⁻¹ and temp. 27 °C)

The adsorption data (Fig. 5) were evaluated using pseudo first order (eqn. 2) and pseudo-second order kinetic model (eqn. 3) [5,11,27] as follows:

$$\log (q_e - q_t) = \log q_t \frac{k_1 - t}{2.303} \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where q_t and q_e (mg g⁻¹) are the amount of metal adsorbed at time t and a state of equilibrium respectively, k_1 and k_2 are the reaction rates constants of pseudo first and second order. The evaluation results with using two the kinetics models show that the adsorption kinetics models of Cu(II) ion on ASC and ASMC tend to follow the pseudo second-order kinetic model (Table-1).

Adsorption isotherms: The effect of initial concentration containing solution of Cu(II) ions to ASC and ASMC in order to determine the patterns of adsorption isotherms and adsorption parameters such as adsorption capacity and adsorption equilibrium constants. Interaction of Cu(II) ions at various concentrations with ASC and ASMC produce a correlation between the concentration of Cu(II) ion with the amount of Cu(II) ions adsorbed (q) on ASC and ASMC (Fig. 6).

TABLE-1
ADSORPTION KINETICS PARAMETERS OF Cu(II) IONS BY THE ASC AND ASMC AT INTERACTION TIME OF 60 min, INTERACTION pH OF 6, AND TEMPERATURE OF 27 °C

Kinetics models		Adsorbents	
		ASC	ASMC
Pseudo first order	k_1 (min ⁻¹)	0.066	0.087
	$q_{e, cal}$ (mmol g ⁻¹)	0.520	0.550
	R^2	0.946	0.940
Pseudo second order	k_2 (g mmol ⁻¹ min ⁻¹)	0.406	0.824
	$q_{e, cal}$ (mmol g ⁻¹)	0.449	0.824
	R^2	0.973	0.988

TABLE-2
ADSORPTION ISOTHERM PARAMETERS OF Cu(II) IONS ON ASC AND ASMC AT INTERACTION TIME OF 60 min, INTERACTION pH OF 6, AND TEMPERATURE OF 27 °C

Models	Parameters	Adsorbents	
		ASC	ASMC
Langmuir	q_{exp} (mg g ⁻¹)	56.400	94.400
	q_m (mg g ⁻¹)	57.769	105.910
	$K_L \times 10^{-4}$ (L mg ⁻¹)	3.530	4.236
	R^2	0.994	0.997
Freundlich	K_f (mg g ⁻¹)	3.548	6.730
	n	1.789	1.686
	R^2	0.789	0.670

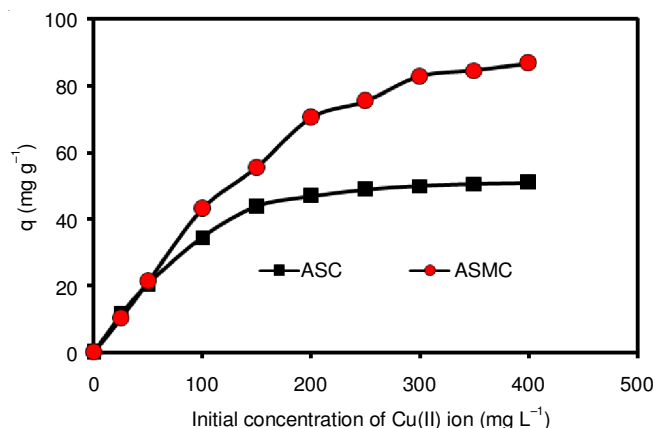


Fig. 6. Relationship between initial concentration of Cu(II) ion and amount of Cu(II) ion adsorbed (q) on ASC and ASMC (pH = 6, interaction times = 60 min and temperature = 27 °C)

Adsorption of Cu(II) ion on ASC and ASMC were evaluated by Langmuir (eqn. 4) and Freundlich adsorption isotherm models (eqn. 5) [5,11] as follows:

$$\frac{t}{q_e} = \frac{1}{q_m K_L C_e} + \frac{1}{q_m} \tag{4}$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{5}$$

where C_e (mg L⁻¹) is the equilibrium concentration of metal ion solution, q_e (mg g⁻¹) is a metal ion adsorption capacity at equilibrium, q_m is the monolayer adsorption capacity of adsorbent, and K_L is the adsorption energy constants.

Freundlich empirical equation is an equation based on heterogeneous surfaces, where K_f is the adsorption capacity factor and n is the intensity factor with the values of n ranges of 1-10 [27]. Furthermore, plot $\log q_e$ versus $\log C_e$ will produce K_f and the exponent of n . Adsorption data of Cu(II) ions on the adsorbent ASC and ASMC obtained from the analysis results using Langmuir and Freundlich equations is presented in Table-2.

Data regression coefficient (R^2) of adsorption isotherm model of Cu(II) ion by ASC and ASMC (Table-2) show that the adsorption process of these metal ions tend to follow the Langmuir adsorption isotherm model. In the Langmuir adsorption isotherm model, R^2 value is closer to 1 than the Freundlich adsorption isotherm model.

Langmuir adsorption isotherm model assume that on the adsorbent surface exists a certain number of active sites which are proportional to the surface area, the adsorbent surface is

uniform and the process is monolayer adsorption [28,29]. Thus, it can be stated that the adsorption process that occurs dominated by chemical interaction between metal ions and the active sites of adsorbent.

Adsorption competition of metal ion pair (binary system):

Adsorption competitions of Cu(II) ions on ASC and ASMC were studied with doing the interaction between pairs of ions Cu(II)/Ni(II), Cu(II)/Zn(II), Cu(II)/Cd(II) and Cu(II)/Pb(II) in solution. These metal ions were selected based on the difference of ionic radii [30]. Besides, differences in the acidity of the metal ions tend to be acidic medium (borderline) and soft acids. From the data, competition of Cu(II) ion with ion pair of Ni(II), Zn(II), Cd(II) and Pb(II) in solution (Fig. 7) can be observed that in general ASMC adsorbent can adsorb all metal ions with fairly high percentage, although between the metal ion pairs competed have different sizes ionic radii. Differences radius of metal ions which competed in the adsorption process is one of the determining factors of the selectivity of an adsorbent to metal ions [31,32]. This indicates that the ASMC is not selective for the metal ions competed. This result was similar with *Sargassum duplicatum* biomass modified adsorbents with a silica matrix which is capable to adsorb Pb(II), Cu(II), and Cd(II) ions with a relatively equal adsorption capacity [33]. This is due to the interaction between metal ions and the active group of adsorbents that occur is dominated by chemical interactions through the formation of a complex between metal ions and functional groups of algae biomass that act as electron

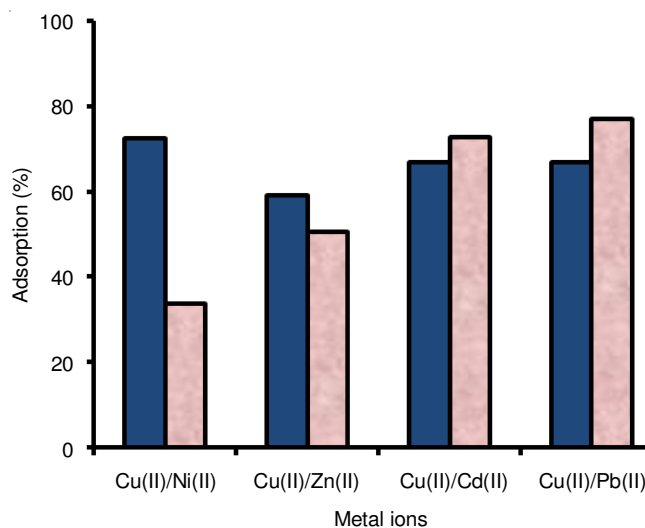


Fig. 7. Adsorption competition of Cu(II) ion to Ni(II), Zn(II), Cd(II) and Pb(II) ions on ASMC

pair donors [34]. Thus, it can be stated that the ASMC adsorbent can be used in the treatment of waste containing a mixture of multi-component metal because it is not selective for the particular metal.

Conclusion

Modification of *Chaetoceros* sp. algae biomass material through the silica-magnetite coating technique has been successfully carried out and tested the adsorption ability to Cu(II) ions in solution. This material has the adsorption rate and capacity greater than algae biomass-silica hybrid material. The modified material can be used as an effective adsorbent to absorb metal ions in a multi-component mixture, because it is not selective for the particular metal.

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