Short Communication:

Kinetic Study of Fulvate Complex Dissolution of Fe, Mn, Zn, Cu, Ni, and Mo from Hydrolyzed Rice Hush Ash Composite (CSH) and Evaluation of Its Performance in Increasing Essential Micronutrient Content in Cempo Merah and Cempo Putih Rice

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Abstract: *This study aimed to make humic composite (CSH), a humus-like material that serves as synthetic humus, that can function as a source of micronutrients in the soil and carry micronutrients to plants through the formed fulvate complex. Qualitative analysis of the micronutrient content of Fe, Mn, Zn, Cu, Ni, and Mo had been carried out using EDX, XRF and ESR spectroscopies, while quantitative analysis was carried out through atomic absorption spectrometry and UV-vis spectrophotometry of fulvic acid and humic acid in CSH. Quantitative analysis was carried out to determine micronutrient content in composite and rice samples using AAS. The results showed that the micronutrient content of Fe, Mn, Zn, Cu, Ni, and Mo in Cempo Putih and Cempo Merah rice applied with CSH was significantly higher compared to commercial rice. The desorption test of Fe, Mn, Zn, Cu, Ni, and Mo from the composite at various pH showed that the optimum pH for desorption occurred at pH 5. The desorption kinetics of Fe, Mn, Zn, Cu, Ni, and Mo from the composite followed a pseudo-second-order kinetic model. Analysis ESR showed that the paramagnetic fulvate complexes detected were only Fe complexes and Mn complexes.*

Keywords: *synthetic humus; fulvate complexes; kinetics; desorption; essential micronutrients*

■ INTRODUCTION

Data from the Central Statistics Agency (BPS-Statistics Indonesia) [1] shows that the amount of rice produced in Indonesia is 30.9 million tons in 2023. However, the need for rice in Indonesia reaches 35.7 million tons or in other words, there is a shortage of rice needs of 13.45%. The lack of supply and nutritional content in rice has an impact on high rates of hunger and stunting. Rice from local and imported production has a low content of essential micronutrients Fe, Mn, Zn, Cu, Ni, Mo and other nutrients, resulting in stunting. Stunting can cause growth failure and inhibit cognitive and motor development, thus affecting brain development and suboptimal physical body size [2]. According to data from the Ministry of Health of the Republic of Indonesia, the prevalence of stunting in Indonesia in 2022 was 21.6%, much higher than the 2024 target (14%) [3] and the minimum target set by the World Health Organization (WHO) (20%) [4].

One of the main factors causing this problem is the low fertility and micronutrient content of soil in Indonesia. Living things need various essential micronutrients, including copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), nickel (Ni), zinc (Zn), boron (B), and chlorine (Cl) for optimal growth [5-6]. Micronutrient deficiencies significantly impact plant productivity, resulting in a lack of nutrition for human health [7-8]. According to data from the Food and Agriculture Organization, micronutrient deficiencies cause a phenomenon called "Hidden Hunger", a condition caused by a lack of micronutrients that are essential for basic physiological functions such as metabolism, growth, and development.

Fe is an essential element for almost all living organisms as it participates in metabolic processes such as DNA synthesis, respiration, and photosynthesis [9]. Mn is an essential micronutrient for plant growth and development and plays a role in plant cell metabolism [10], while in humans, Mn acts as an enzyme cofactor for various enzymes [11]. Zn is an important micronutrient for humans and plants. In humans, Zn is involved in various physiological processes, including immune function, protein synthesis, and DNA synthesis [12] In humans, Cu plays a role in the formation of red blood cells and maintaining the balance of the body's immune system [13], while in plants Cu plays a special catalytic role that is important for leaf development, disease resistance, and fertility [14-16]. In plants, Ni is involved in various metabolic processes including urea hydrolysis in plant tissues and the active site of the urease enzyme, while in humans Ni is involved in various metabolic processes, including cellular redox states and biochemical and physiological functions [17-18]. Mo plays a role in nitrate reduction and nitrogen fixation in plants. In humans, Mo acts as a cofactor in several enzymes, including sulfite oxidase, which converts sulfite to sulfate, and xanthine oxidase, which is involved in purine metabolism in digestion process [19].

One strategy to overcome the decline in agricultural productivity is to improve the quality of soil organic matter and micronutrients through soil fortification with the addition of humus. Humus itself is naturally created from the process of decomposing plant or animal remains that are decomposed by microorganisms, a process known as humification [20]. However, the process of forming humus takes a long time and is considered less environmentally friendly because the process produces significant amounts of CO_2, water vapor, and nitrogen oxide emissions [21-22]. According to Tan [23], the humification process can be carried out not only microbiologically but also chemically with a faster process.

In our previous work, Kuncaka [21] proposed slow release organic paramagnetic (SROP) fertilizer or synthetic humus based on the New Road of Synthetic Humification scheme (Patent Number IDP00201401530) by combining the concept of humus as a supramolecule [24] and the concept of *Terra Preta de Indios* [25] through the hydrothermal carbonization (HTC) process [20]. This synthetic humus was developed with similar characteristics to natural humus and functions as a slow-release agent for macronutrients and micronutrients. In addition, it can play a role in regulating electron transfer, controlling water content, and increasing organic matter content in the soil.

Biomass that can be used as raw material for making synthetic humus is chicken feather waste and rice husk ash. Chicken feathers contain 92.00% keratin, 1.02% carbohydrates, 1.28% lipids, and 0.69% water [26]. Keratin has a high protein and amino acid content so it can be a source of nitrogen [27-29]. Kuncaka et al. [29] also reported that chicken feather waste, through a combination of HTC and phosphorylation processes, can produce chicken feather hydrolysate containing humic acid, fulvic acid, and humin with a humus-like structure. In addition, rice husk ash has a silica content of 85–90%, and chemical elements such as P, K, Ca, Fe, Cu, Mn, Mo, Zn, and Ni and is moderately basic and has a moderately high neutralizing ability so it can be applied as fertilizer [30-33]. In this study, it was reported that the combination of rice husk ash containing micronutrients with the liquid fraction of chicken feather hydrolysate as synthetic humus, carrier agent, and micronutrient chelator can produce a composite that is rich in humus and plays an important role as a source of micronutrient fortification that has the potential to be an anti-stunting agent.

■ EXPERIMENTAL SECTION

Materials

The materials used in this study were humic composite (CSH), Cempo Putih rice, and Cempo Merah rice from CV Humus. Merck production materials consist of nitric acid (HNO_3), perchloric acid ($HClO_4$), and stock solution of Fe, Mn, Zn, Cu, Ni, and Mo. Other materials include distilled water, filter paper, universal pH, and BULOG SPHP Rice.

Instrumentation

The tools used in this study include a set of glassware, magnetic stirrer, hot plate, shaker, pH meter, analytical balance, atomic absorption spectroscopy (AAS, Analytik Jena ContrAA 800), scanning electron microscopy (SEM/EDX, JED 230), X-ray fluorescence (XRF, Rigaku), and electron spin resonance (ESR, TDS 10001B).

Procedure

CSH application on rice plant

CSH application on rice plants was conducted by CV Humus on farmland located at Pakisaji, Candibinangun, Pakem, Sleman, Yogyakarta Special Region (–7.6669251, 110.3962871). The area of land used in this planting was 1000 m^2. Cempo Putih and Cempo Merah rice varieties were planted with CSH application without chemical fertilizers. Meanwhile, Bulog SPHP commercial rice was used to compare essential micronutrient content. CSH was applied 10 and 25 d after transplanting, with a dose of 10 kg for each application, and the total dose was 20 kg/1000 m^2.

Characterization and analysis

The CSH characterization process was conducted using EDX, XRF, AAS, and ESR, while the characterization of Cempo Merah, Cempo Putih, and commercial rice was conducted using EDX, XRF, and AAS. EDX and XRF characterization were conducted to determine the element content in CSH qualitatively. AAS analysis was performed to quantitatively determine the micronutrient content of Fe, Ni, and Zn. ESR characterization was performed to analyze the content of paramagnetic materials dissolved in CSH.

EDX and AAS characterization were conducted at the Integrated Research and Testing Laboratory of Gadjah Mada University, XRF characterization was conducted at the Inorganic Chemistry Laboratory FMIPA Gadjah Mada University, and ESR characterization was conducted at the Advanced Physics Laboratory FMIPA Brawijaya University.

Analysis of micronutrient content of Fe, Mn, Zn, Ni, Cu, and Mo in CSH by AAS

Determination of micronutrient content of Fe, Mn, Zn, Cu, Ni, and Mo was carried out by wet deconstruction method using HNO_3 and $HClO_4$ solutions. CSH samples were taken at as much as 0.5 g and then put into a 50 mL beaker glass. Then, 5 mL of 65% HNO_3 and 1 mL of 70–72% $HClO_4$ were added. The solution was heated at a gradual temperature up to 200 °C until it became clear. The solution was then cooled and filtered. The filtrate obtained was then put in a 25 mL volumetric flask, diluted with distilled water, and analyzed using AAS.

Analysis of micronutrient content of Fe, Mn, Zn, Ni, Cu, and Mo in Rice samples

Determination of the micronutrient content of Fe, Mn, Zn, Cu, Ni, and Mo was carried out by wet deconstruction method. Rice samples were weighed as much as 0.5 g in a beaker glass, then 5 mL of 65% HNO_3 was added and allowed to stand for one night in an acid chamber. After that, the sample was added with 5 mL of 65% HNO_3 and 1 mL of 70–72% $HClO_4$ and heated gradually to 200 °C. The solution is heated until it changes color to clear. The solution was then cooled and filtered. The filtrate obtained was then put in a 25 mL volumetric flask, diluted with distilled water, and analyzed using AAS.

Desorption test

Effect of pH. CSH weighed as much as 2.5 g was put into 6 bottles, added with 25 mL of distilled water which varied pH 2, 3, 4, 5, 6, 7, and 8. The bottle was shaken for 180 min. The solid and solution were separated by filtering. The filtrate was then measured for Fe, Mn, Zn, Cu, Ni, and Mo concentrations using AAS. The study was conducted at ±25 °C and ±1 atm.

Effect of time. CSH was weighed as much as 2.5 g and then put in a bottle, added with 25 mL of distilled water with optimum pH level. The bottle was shaken for 60, 180, 360, 720, 960, and 1440 min. The solid and solution were separated by filtering. The filtrate was then measured for Fe, Mn, Zn, Cu, Ni, and Mo concentrations. The study was conducted at ±25 °C and ±1 atm.

■ RESULTS AND DISCUSSION

Qualitative Analysis

Based on the results of the analysis using EDX, the qualitative content of the CSH composite and rice was detected in the form of microelements (Fe, Mn, Zn, Cu, Ni). XRF analysis obtained the content of Fe, Mn, Zn, Cu, Ni, and Mo. Micronutrient Mo was only detected using XRF instrument because it has higher sensitivity compared to EDX. XRF instruments are used for larger area analysis with lower spatial resolution, while EDX can be used for microanalysis and can analyze smaller areas with higher spatial resolution [34].

Quantitative Analysis

The quantitative analysis results are listed in Table 1. The results show that CSH composite contains Fe, Mn, Zn, Cu, Ni, and Mo. Based on the Decree of the Minister of Agriculture of the Republic of Indonesia Number 261/KPTS/SR.310/M/4/2019 [35] concerning the minimum technical requirements for organic fertilizers, biological fertilizers, and soil conditioners, the maximum required micronutrient content of Fe, Zn, and Ni (Mn, Cu, and Mo are not required) is 15,000, 5,000, and 50 ppm, respectively. The analysis showed that CSH met the requirements because the contents of Fe, Zn and Ni were below the maximum value based on the Decree of the Ministry of Agriculture of the Republic of Indonesia.

The results of UV-Vis spectrophotometric analysis of CSH according to patent number IDS000006209 [36] containing fulvic acid of 1.26%, where the fulvic acid content is greater than humic acid, so in this study, it is assumed that the potential ability of fulvic acid as a ligand is able to bind nutrients in complex form, compared to humic acid to carry micronutrients from the soil surface to plants. In addition, the molecular size of fulvic acid is smaller than that of humic acid, and the lipophilic nature of fulvic acid is much greater than that of humic acid. Therefore, it is feasible that fulvic acid is more responsible for the diffusion of micronutrients from soil to plants.

Table 2 shows that the micronutrient content in Cempo Merah and Cempo Putih rice has a higher content compared to commercial rice, but still below the threshold required by WHO [37-41]. Therefore, it can be said that CSH can be a source of micronutrients and produce fulvic acid complexes that are able to carry micronutrients, so the CSH-applied rice has the potential to overcome the problem of stunting caused by “Hidden Hunger” from micronutrient deficiencies.

Paramagnetic Content Analysis

The results of the analysis of the content of paramagnetic compounds in the dissolved CSH composite are presented in Fig. 1, using ESR on the dissolved complex from pH 2 to 8 which consistently shows only the Fe^{3+} fulvate complex and the Mn^{4+} fulvate complex. This is because these two complexes are quite large in the solution while other micronutrients are not detected.

From the results of the ESR resonance curve analysis, the g-factor value was obtained in the Fe^{3+} fulvate complex and the Mn^{4+} fulvate complex with pH

Table 1. AAS analysis results of micronutrient content in CSH composite

Micronutrient	Value (ppm)	Maximum limit value (ppm)*
Fe	358.14 ± 1.59	15000
Mn	122.69 ± 0.76	-
Zn	68.95 ± 0.78	5000
Cu	63.25 ± 1.22	-
Ni	44.33 ± 0.26	50
Mo	12.82 ± 0.09	-

*Based on the Decree of the Minister of Agriculture of the Republic of Indonesia Number 261/KPTS/SR.310/M/4.2019

Table 2. AAS analysis results of micronutrient content in CSH-applied rice (Cempo Putih, Cempo Merah) and commercial (BULOG) rice

Micronutrient	Concentration (ppm)			Rice threshold (ppm)
	Cempo Putih	Cempo Merah	Commercial	
Fe	17.95 ± 0.36	15.13 ± 0.35	11.55 ± 0.63	48.00
Mn	1.68 ± 0.01	2.25 ± 0.09	1.32 ± 0.03	44.58
Zn	3.69 ± 0.18	5.46 ± 0.40	2.63 ± 0.08	50.00
Cu	2.73 ± 0.02	2.54 ± 0.01	1.74 ± 0.02	20.00
Ni	2.98 ± 0.22	4.65 ± 0.12	1.91 ± 0.18	67.90
Mo	0.33 ± 0.01	0.51 ± 0.01	0.25 ± 0.01	1.00

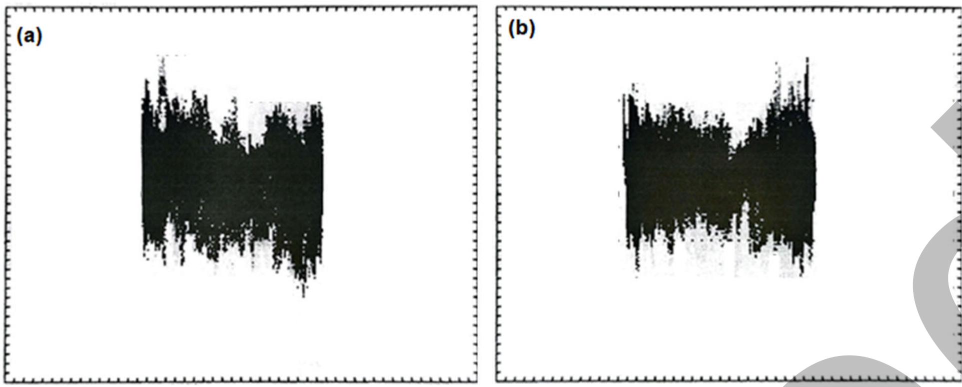


Fig 1. ESR resonance curve for (a) fulvate Fe^{3+} complex and (b) fulvate Mn^{4+} complex

variation dissolution containing paramagnetic compounds. The g-factor value was obtained with a complex value of 1.7679 and 1.8676. According to Juswono et al. [42], these values indicate the Fe^{3+} and Mn^{4+} compounds, respectively. These compounds can be detected well in ESR because of their relatively large content, this condition shows that CSH is able to act as an SROP material [43].

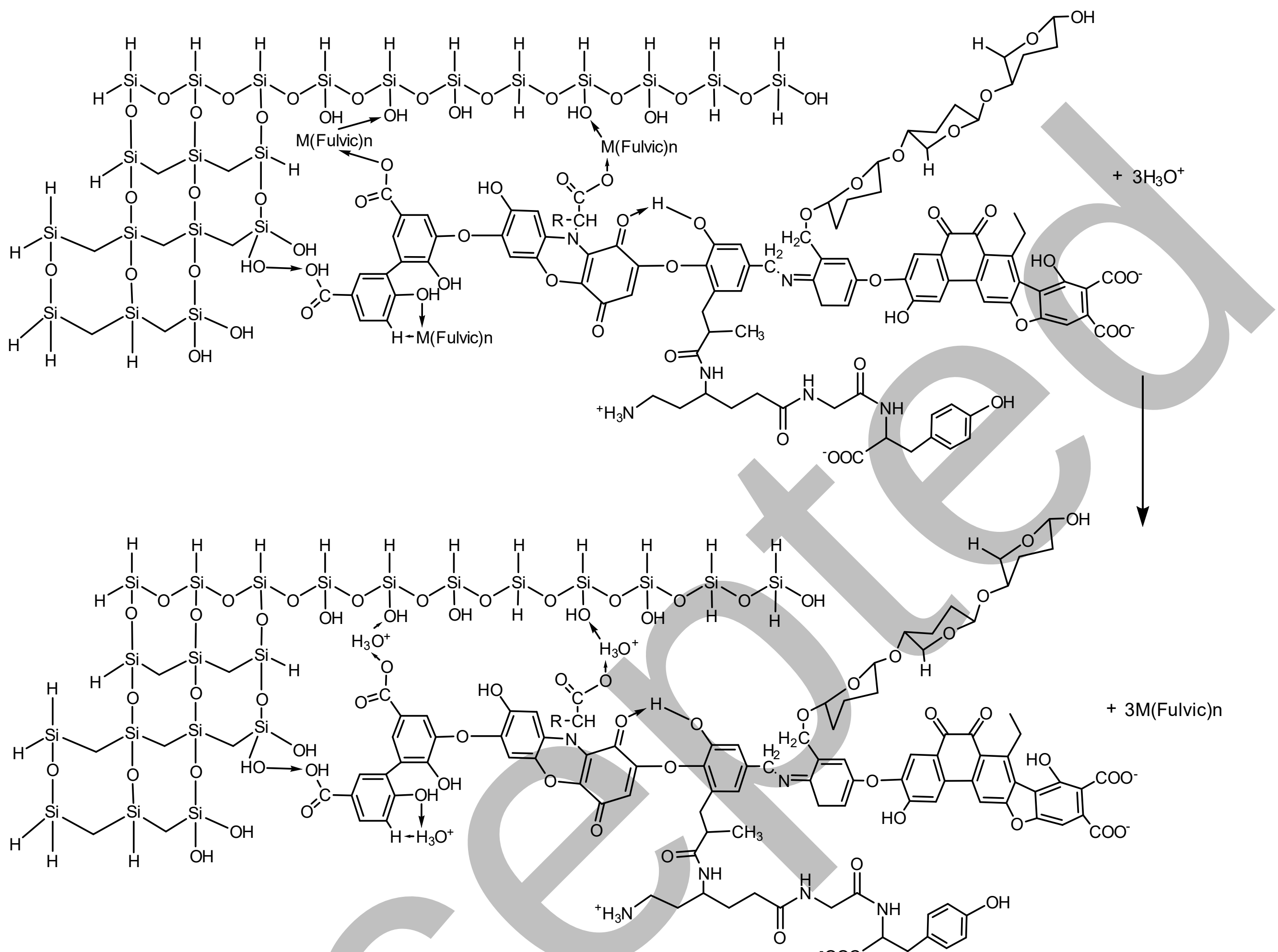
Mechanism

Qualitative and quantitative analysis results show that CSH contains micronutrients Fe, Mn, Zn, Cu, Ni, and Mo which can be a source and carrier of micronutrients that have been chelated to plant roots. Therefore, CSH can be used as a soil improver that can increase soil productivity. From UV-vis spectrophotometer analysis, CSH or humus like (synthetic humus) contains humic acid and fulvic acid of 0.09 and 1.26%, respectively. The greater content of fulvic acid has the ability as a ligand that is able to bind nutrients in a complex form known as chelate. These chelates help store nutrients in the soil and release them gradually when plants need them. This ability is very useful in increasing the availability of nutrients for plants and improving soil quality. The ability to chelate metal elements in humic substances is inseparable from the presence of carboxylic (–COOH) and phenolic (–OH) groups in the structure of humic and fulvic acids [44-45]. These groups will dissociate to form a negative charge on the micronutrients in CSH that can chelate metals [46].

Chelating compounds of the humus substances in CSH with elements such as Fe, Ni, and Zn can lead to increased solubility and availability of these metals to plants under certain conditions. The chelating compounds "hold" the metals in the soil solution, and as a consequence, they can easily diffuse them to the plant roots. This may be due to the special ring structure of chelate compounds, where the metal ion is surrounded by molecules such as fulvate compounds. It can either be released from the chelate structure and enter the root or penetrate in the chelate form and disintegrate in the root. In both mechanisms, organic molecules are "returned" to the CSH solution and soil, which can then chelate the next metal cation. The hypothetical structure of micronutrient release from CSH is shown in Fig. 2.

Desorption Test for Variation of pH and Time

Desorption test was conducted to determine the release of Fe, Mn, Zn, Cu, Ni, and Mo ions from fulvate-substance composites. Fig. 3 shows that Fe, Mn, Zn, Cu, Ni, and Mo ions in the CSH sample dissolved in the entire pH range observed (2–8). The amount of dissolved ions decreased relatively until pH 4 and then experienced a slight increase at pH 5. It can be concluded that the optimum desorption occurs at pH 5. Thus, phenomena indicate that the charge of ionic of the metal-fulvate complex becomes more neutralized by hydroxyl ion to form a complex metal-fulvate hydroxide neutral. The largest desorption process occurs at acidic environment due to competition between H^+ ions and Fe, Mn, Zn, Cu, Ni, and Mo ions. At lower pH, H^+ ions compete to bind to carboxyl groups on the surface of CSH as a result iron, nickel, and zinc ions will be released from the active side of CSH and replaced by H^+ ions. This



M= Micronutrients (Fe, Mn, Zn, Cu, Ni, and Mo)

Fig 2. Hypothetical structure of micronutrient release from CSH

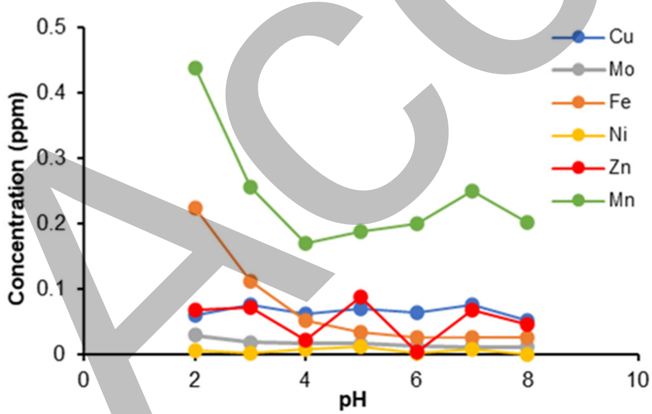


Fig 3. Effect of pH on micronutrient desorption

is consistent with the research of Boguta et al. [47], which states that Fe metal is more available at pH 5 because in the pH 6–8 range, iron metal is bridged with humic acid to form insoluble iron hydroxide, so that the amount of dissolved iron metal is less in pH 6–8 conditions than in pH 5 conditions. The availability of Mn micronutrients for plants depends on pH, at pH ≤ 5.5 Mn ions dissolve in the soil [48]. The solubility of Zn is also affected by pH, an increase in soil pH, especially above 6.5 will cause a decrease in the solubility and availability of soil Zn for plants [49]. Research from Bhalerao et al. [50] stated that Ni is more soluble at acidic pH than at neutral to alkaline pH because metal ions can become insoluble hydroxides in an alkaline environment. According to Thapa et al. [51], micronutrient Cu is usually available at pH 5. Mo will dissolve easily at pH 5–6 [19]. From the data, it can be concluded that essential micronutrients can be desorbed relatively stable at pH 5.0.

To study the desorption kinetics of essential micronutrients, micronutrient dissolution was studied at

Table 3. Comparison of micronutrient desorption kinetics models

Kinetics model	Parameter	Micronutrients					
		Fe	Ni	Zn	Mn	Cu	Mo
First-order	R^2	0.9058	0.9355	0.9144	0.8644	0.9599	0.9427
	K (h^{-1})	0.0002	0.0008	0.0024	0.0024	0.0016	0.0005
Second-order	R^2	0.9060	0.9346	0.9189	0.8624	0.9614	0.9425
	K (h^{-1})	0.0306	0.0009	0.0025	0.0012	0.0017	0.0044
Pseudo-first-order	R^2	0.9844	0.9464	0.9524	0.8304	0.9879	0.8161
	K (h^{-1})	0.1400	0.1738	0.0821	0.0348	0.1032	0.0719
Pseudo-second-order	R^2	0.9936	0.9912	0.9782	0.9185	0.9914	0.9824
	K (g mg^{-1} h^{-1})	7.5650	9.2680	2.6400	1.3950	5.9060	2.9920

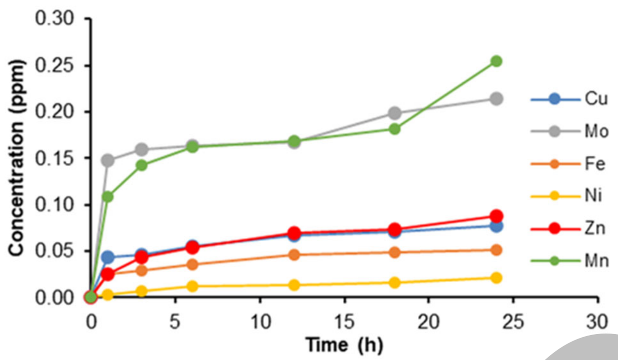


Fig 4. Effect of time on micronutrient desorption

various times under pH 5.0 conditions. The desorption test in Fig. 4 was carried out for a time variation of 60, 180, 360, 720, 960, and 1440 min. The desorption results of the time variation showed that the longer the contact time between the composite and distilled water, the more Fe, Mn, Zn, Cu, Ni, and Mo ions were released into the distilled water. Then several kinetics models were obtained as in Table 3.

The kinetic models studied to determine the Fe, Mn, Zn, Cu, Ni, and Mo release rates are first-order reaction kinetics, second-order reaction kinetics, pseudo-first-order reaction kinetics, and pseudo-second-order reaction kinetics. Determination of the desorption kinetics model was done by the graphical method by looking at the coefficient of determination (R^2) value of each graph plot summarized in Table 3. Based on Table 3, it can be seen that the appropriate Fe, Mn, Zn, Cu, Ni, and Mo desorption kinetics model with an R^2 value closest to 1 is a pseudo-second-order kinetics model. This is in accordance with research conducted by Zhang et al. [52] which states that metal desorption from humic compounds is found that the desorption kinetics follow a pseudo-second-order kinetic model.

■ CONCLUSION

Based on the results, fulvic substances and micronutrients in CSH can be used as a source and carrier of micronutrients Fe, Mn, Zn, Cu, Ni, and Mo for the purpose of agronomic fortification. Agronomic fortification with CSH can increase the micronutrient content of Fe, Mn, Zn, Cu, Ni, and Mo in Cempo Putih and Cempo Merah rice. The optimum desorption of fulvic substances complexes of micronutrients Fe, Mn, Zn, Cu, Ni, and Mo from CSH occurred at pH 5. The desorption kinetics of fulvate complexes of essential micronutrient metals Fe, Mn, Zn, Cu, Ni, and Mo from CSH followed a pseudo second-order kinetics model.

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■ CONFLICT OF INTEREST

The authors did not have any conflict of interest to declare.

■ AUTHOR CONTRIBUTIONS

Agus Kuncaka is the supervisor with the main idea and conceptualization of this research. Andika Rifqi Rayendra, Dilla Karuniawati, Rifka Ayu Kurniawati, as research assistants collected the experimental data. Dwi

Siswanta, Mudasir, and Adhitasari Suratman analyzed the data.

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