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Use of Monosodium Glutamate (MSG) for Green Leaching Process: An Overview

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ABSTRACT

Monosodium glutamate (MSG) is a sodium salt of glutamic acid, a type of amino acid occurred naturally in some type of foods. MSG has the chemical formula of $C_5H_8NO_4Na$-NH_2, which is used mainly as flavour enhancer. In mineral processing, MSG has been tried as lixiviant in base metals leaching from secondary sources such as Zn and Cu from electric arc furnace dust and Li and Co from spent lithium-ion battery cathode. The efficacy of base metal leaching using glutamate is mainly contributed by the ability of glutamate to form metal complex especially in alkaline leaching conditions. Leaching in alkaline conditions also pose advantage in terms of leaching selectivity. Fouling elements such as Fe, Al, Mg and Ca are selectively enriched in solid residue. However, further research is needed to establish the optimal leaching conditions using MSG as lixiviant. This review paper will discuss the research direction in hydrometallurgical metal extraction using MSG, including possible improvements and disadvantages.

Keywords: monosodium glutamate; reagent; leaching; extraction.

INTRODUCTION

Monosodium glutamate (MSG) or is the sodium salt of glutamic acid, which is one of the most abundant non-essential amino acids. This amino acid naturally occurred in several type of foods (Table 1). MSG has the chemical formula $C_5H_8NO_4Na$-NH_2 (Figure 1) which has a melting point of 232°C or 505 °K and the ability to strengthen active compounds (Löliger, 2000). MSG has been widely consumed worldwide as a food flavor enhancer. MSG has a crystalline powder-like form that is white color, easily soluble, and odorless.

The average consumption of MSG in European countries are 300-500 mg/day/capita with the highest intake of 1000 mg/day. The intake in Asian countries is 1200-1700 mg/day with the highest intake being 4000 mg/day (Beyreuther, 2006).

OVERVIEW OF MONOSODIUM GLUTAMATE FOR LEACHING

MSG has been tested in several studies to extract base metal by leaching process. Based on previous research, MSG can affect metal recovery and selectivity of Zn and Cu leaching over other elements. The optimum conditions for Zn and Cu leaching recovery from electric arc furnace dust occurred at alkaline condition (pH 9), MSG concentration between 0.1 M and 2 M, pulp density 50 g/L, and leaching time of 12 hours at room temperature

Table 1. Natural Glutamate Content in Food Ingredients (Mg/100 g Ingredients) (Löliger, 2000).

Food Material	Glutamate	Free Glutamate
Milk and Products		
Cow's milk	819	2
ASI	229	22
Parmesan Cheese	9.847	1.200
Poultry		
Egg	1.583	23
Chicken	3.309	44
Duck	3.636	69
Meat		
Beef	2.846	33
Pork	2.325	23
Fish		
Cod	2.101	9
Mackerel	2.282	36
Salmon	2.216	20
Vegetables		
Peas	5.583	200
Corn	1.765	130
Bit	256	30
Carrot	218	33
Onion	208	18
Spinach	289	39
Tomato	238	140
Pepper	120	32

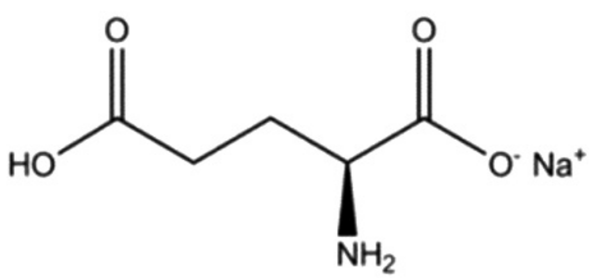

Figure 1. Monosodium Glutamate (MSG) Formula (Löliger, 2000).

(Prasetyo and Anderson, 2020). The minimum MSG concentration for Zn dissolution (in the form of Zn-oxide or hydroxide) is 0.7 M. In the case of Cu, the MSG concentration has a little effect due to the higher Zn concentration in the pregnant leach solution (Figure 2). The leaching process at higher MSG concentrations can increase the recovery of other elements such as Fe due to the formation of soluble complex e.g. $FeGlu^+$. The Figure 2 show the optimum recovery of Zn and Cu was obtained at concentrations of 1.2 and 0.7 M, respectively. At higher MSG concentrations the recovery of other metals, especially Mg and Ca, was substantially increased and hence reduced the leaching selectivity (Prasetyo and Anderson, 2020; Prasetyo et al., 2020).

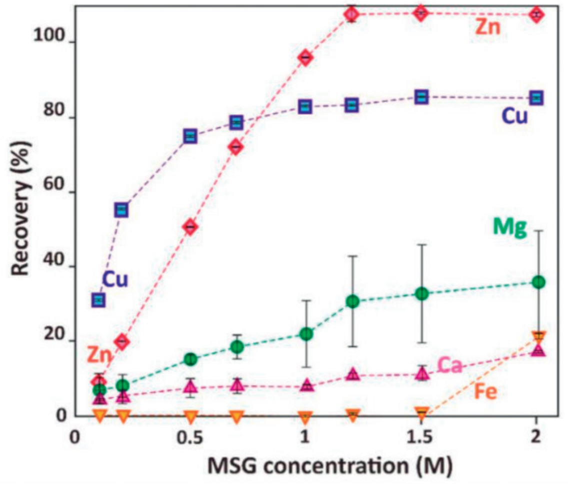

Figure 2. Recovery Zn, Cu, Mg, Ca, and Fe to MSG concentration (Prasetyo and Anderson, 2020; Prasetyo et al., 2020).

Glutamate can be recovered from the spent pregnant leach solution as a glutamic acid precipitate by decreasing the pregnant leach solution pH to 2-4.5. In pH condition less than 2, glutamate precipitate is redissolved through the formation of the soluble cationic species H_3Glu^+. Experimental work has been carried out to recover glutamate from a spent leached solution. The optimum precipitation pH was 3, which at this pH more than 90% of glutamate was recovered as glutamic acid precipitate (Figure 3) (Prasetyo and Anderson, 2020).

Another research is also developed to recover Ni from secondary source electric arc furnace dust using ammonium salt of glutamic acid or monoammonium glutamate (MAG). The study showed that increasing MAG concentration from 0.5; 1; and 1.5 M can suppress the reaction rate of Ni (Prasetyo et al., 2021). This was caused by the increasing of glutamate concentration (added as glutamic acid) can decrease the pH due to neutralization. The pH decreased to 9.5 at glutamate concentrations 0.5 M, to 8.3 and 7.5 at glutamate concentration 1 and 1.5 M, respectively. Decreasing pH then reduced the reaction rate and maximum recovery of Ni (Prasetyo et al., 2021).

When compared glutamate with other reagents such as ammonium hydroxide (NH_4OH), the results showed the addition of these reagents positively affect the reaction rate

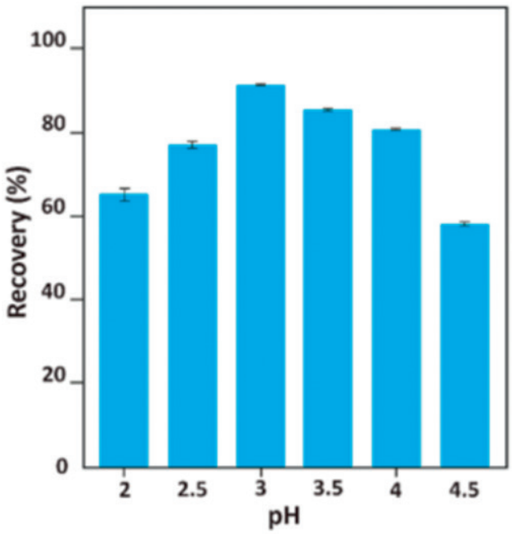

Figure 3. Efficiency of leaching recovery with MSG at various pH (Prasetyo and Anderson, 2020).

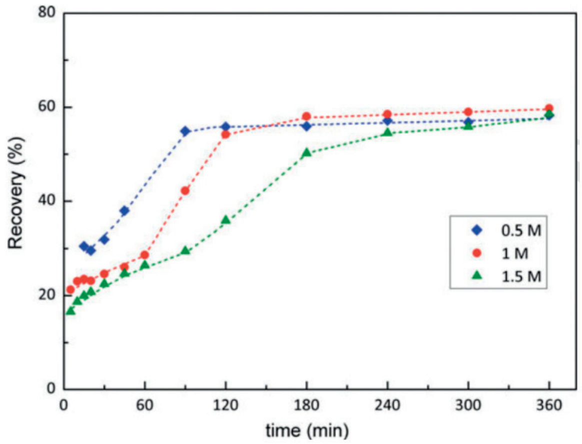

Figure 4. Ni recovery at different MSG concentrations (Prasetyo et al., 2021).

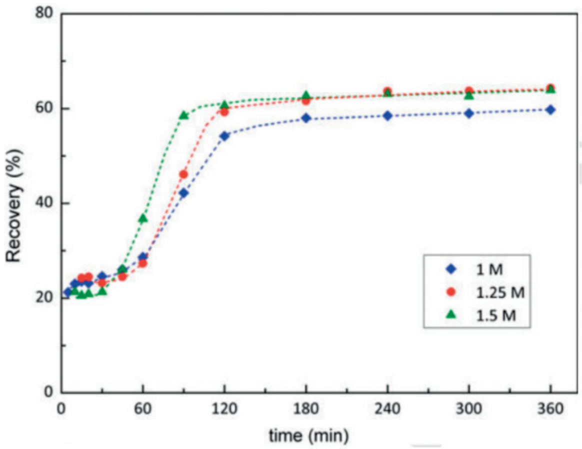

Figure 5. Ni recovery using ammonium hydroxide reagent at different concentrations (Prasetyo et al., 2021).

and the maximum yield of Ni. For example, increasing the ammonium hydroxide concentration will increase the pH from 8.3 for 1 M to 9.2 for 1.25 M and 9.4 for 1.5 M. The effective amount of ammonium hydroxide solution added to the leaching process is determined by the concentration glutamic acid because it is only soluble in weak acids to alkaline pH > 5 (Prasetyo et al, 2021).

In another study, the effect of MSG concentration on copper-glutamate complex formation was studied by varying the glutamate concentrations while copper concentration was kept constant at 100 g/ml (Prasetyo, 2012). It can be seen in Figure 6 that the absorbance has a positive correlation with a molar ratio of glutamate/copper up to 5 and is constant above that value. This shows that the addition of MSG does not significantly affect the absorbance and the molar ratio of the Cu-Glu complex in 1:5. Then it can also be said that the photometric method using MSG as the reagent has a recovery of >82% compared to atomic absorption spectroscopy (AAS) results which are considered as true values. The photometric method using MSG is a technically simple, quantitative, inexpensive, and environmentally friendly method (Prasetyo, 2012).

In the study conducted to determine the effect of glutamate concentration on recovery and selective leaching of Ni, glutamate concentration was varied from 0,1 to 2 M (with constant pH variable 9, liquid/solid ratio 20 ml/g, leaching time 12 hours) (Prasetyo et al, 2021). The results can be seen in Figure 7a which shows that the optimum concentration of glutamate for Ni recovery is 1.5 M with 66% recovery. Increasing the glutamate concentration to 2 M did not significantly increase the leaching efficiency. Recovery can be increased drastically

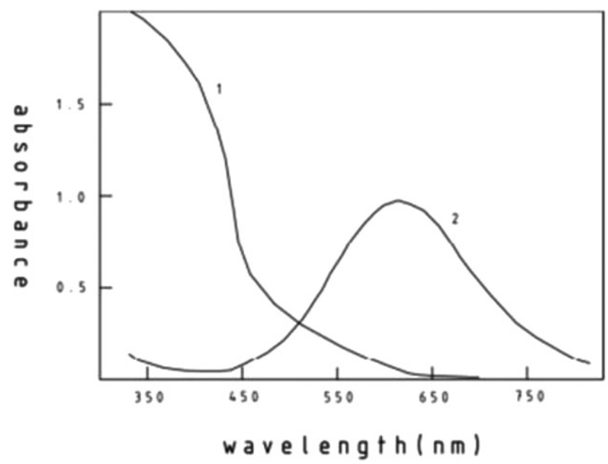

Figure 6. Absorption spectra on Fe(III)-glutamate complex, Fe(III) concentration 500 g/ml, pH 2 and MSG 1.6%. 2-Cu(II)-glutamate complex, copper concentration 200 g/ml, pH 10, MSG 1.6% (Prasetyo, 2012).

due to strong bonding between glutamate, Fe, and the ability of glutamate to partially prevent hydrolysis. However, Figure 7b shows the optimal concentration of glutamate for selective Ni which is 0.5 M ([Ni]/[Al]=226, [Ni]/[Fe]=112, [Ni]/[Ca]=3.5 and [Ni]]/[Mg]=4) (Prasetyo et al., 2021; Brunelli and Dabalà, 2015).

The effect of liquid/solid ratio was studied at 5-30 ml/g, while pH, MSG concentration, and stirring time were set constant at 9, 1 M, and 12 hours, respectively. Figure 8a shows that the optimum solid-liquid ratio for Ni recovery is 15 ml/g (55.3% recovery). A higher liquid/solid ratio does not increase the leaching efficiency. The results in Figure 8b show the decreasing in the liquid/solid ratio that have a positive effect on the selectivity of Ni. This also indicated that the continuous leaching method which is preferred over the batch method (Brunelli and Dabalà, 2015).

Further, research has been carried out to isolate Zn, Cu, and Ni using solvent extraction from glutamate media as a hypothetical product of alkaline leaching of electric

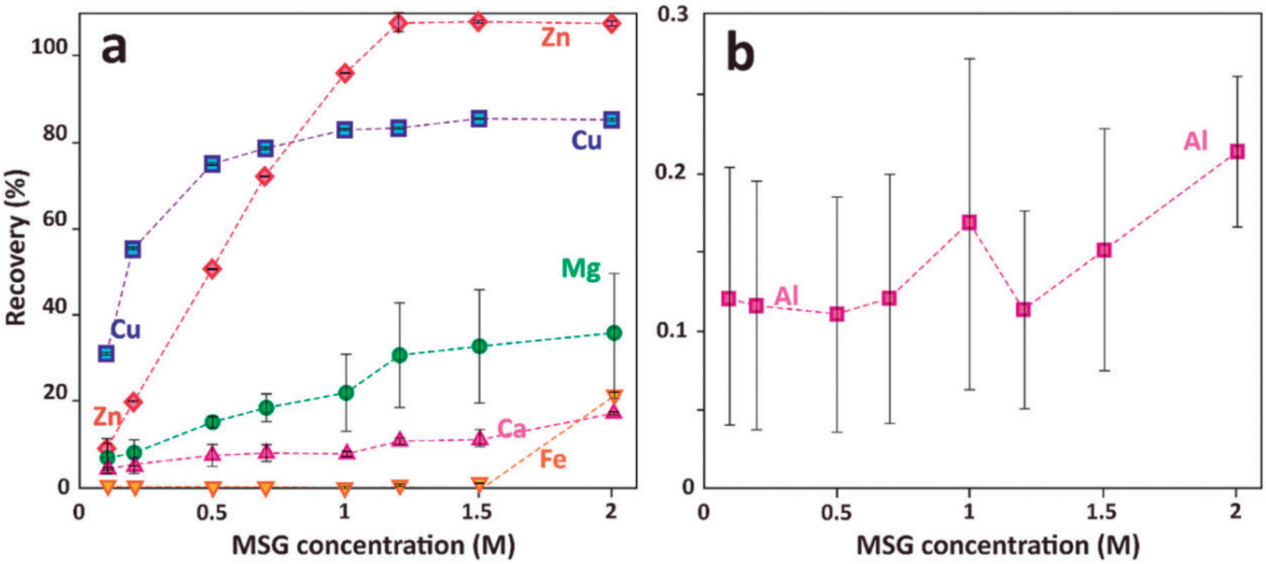

Figure 7. Effect of MSG concentration on metal recovery (a) and selectivity factor (b) (Brunelli and Dabalà, 2015).

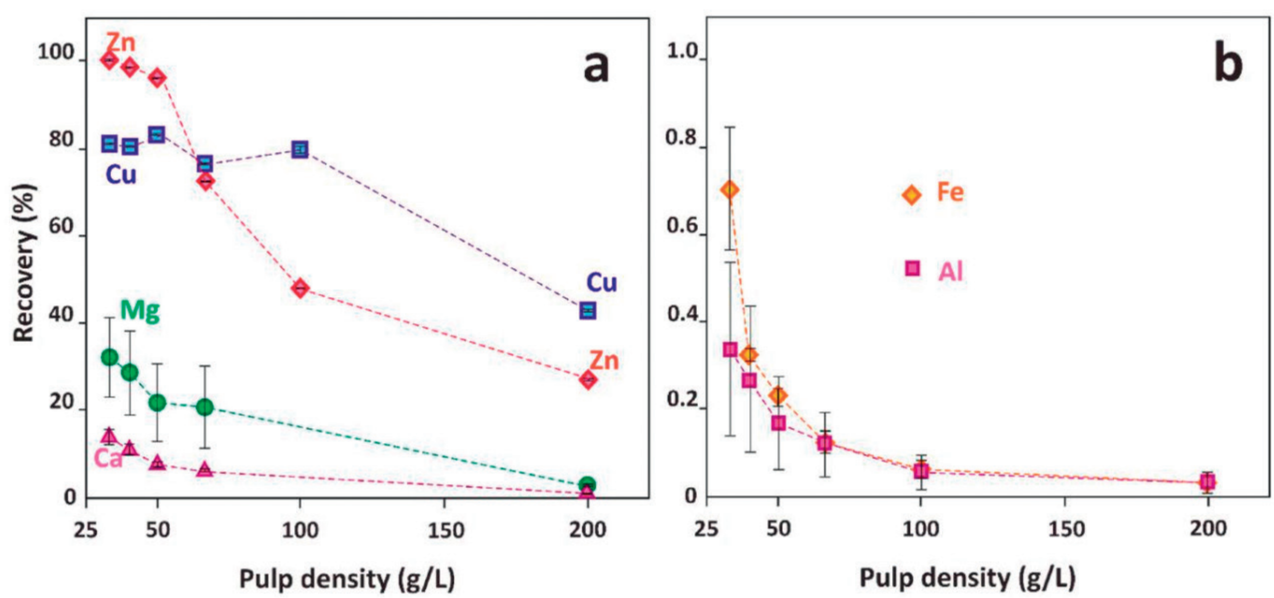

Figure 8. (a) Effect of solid-liquid ratio on metal recovery and (b) Effect of solid-liquid ratio on selectivity factor (Brunelli and Dabalà, 2015).

arc furnace dust. Typical metal concentration in leach solution was 17.6, 0.35, and 0.14 g/L for Zn, Cu and Ni, respectively (Prasetyo et al., 2020). Three commercial extractants were investigated: Cyanex 272, DEHPA, and Acorga M5640, which was selectively used to isolate Zn, Ni, and Cu. In addition to the effect of pH, the parameters studied included the O/A ratio, the concentration of extractant in kerosene as a diluent and the concentration of sulfuric acid as a stripping agent. The pH is the most critical factor in determining the separation factor between the three metals because pH can control metal speciation in the leaching solution and regulate interactions between metal ions and extractants (Prasetyo et al., 2020).

MSG has the chemical formula $C_5H_8NO_4Na$, which is a sodium salt of glutamic acid. This type of glutamic acid is one of the most abundant non-essential amino acids found in nature (Butnariu and Sarac, 2019). Glutamate is considered as a nonvolatile reagent since it poses no negative effect on health when used at low concentrations (Butnariu and Sarac, 2019). The use of MSG as an alternative reagent in metal extraction is relatively recent, hence further studies are needed to recognize its efficacy at industrial scale. Glutamate efficacy in metal extraction is due to its act as tridentate ligand. The hydroxyl, amine and carboxylic group of glutamate hypothetically will coordinate with metal ions, although sometimes the full tridentate coordination fails to achieve (Murphy et al., 2020; Perea et al., 2021). Glutamate-metal coordination depends heavily on pH. Glutamate can exist in solution as a glutamate cation ($H_3(glu)^+$, $H_2(glu)^+$), zwitterion (H(glut)), and glutamate anion (Glu^-), as depicted in Figure 10.

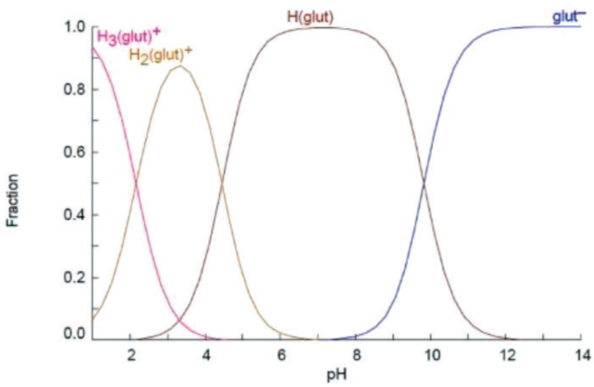

Figure 9. Flowsheet on the recovery of Zn, Cu, and Ni from glutamate media (Prasetyo et al., 2020).

Previous research has been carried out on several parameters affecting metal recovery using MSG as leaching reagent, including pH on Zn recovery, which was studied at range 8-10 (Prasetyo et al., 2021). The constant variables in the pH study included MSG concentration (1 M), pulp density (20 ml/g), and leaching time (12 hours). The results in Figure 11 shows than Zn recovery will increase when pH increases from 8 to 9, and further decreases at pH higher than 9 (Prasetyo et al., 2021).

In addition to pH, there are other effects such as the effect of MSG concentration in which the concentration range tested was from 0.5 to 1 M. The constant variables in this test including, pH 9, pulp density of 20 mL/g, and leaching time for 12 hours. The results in Figure

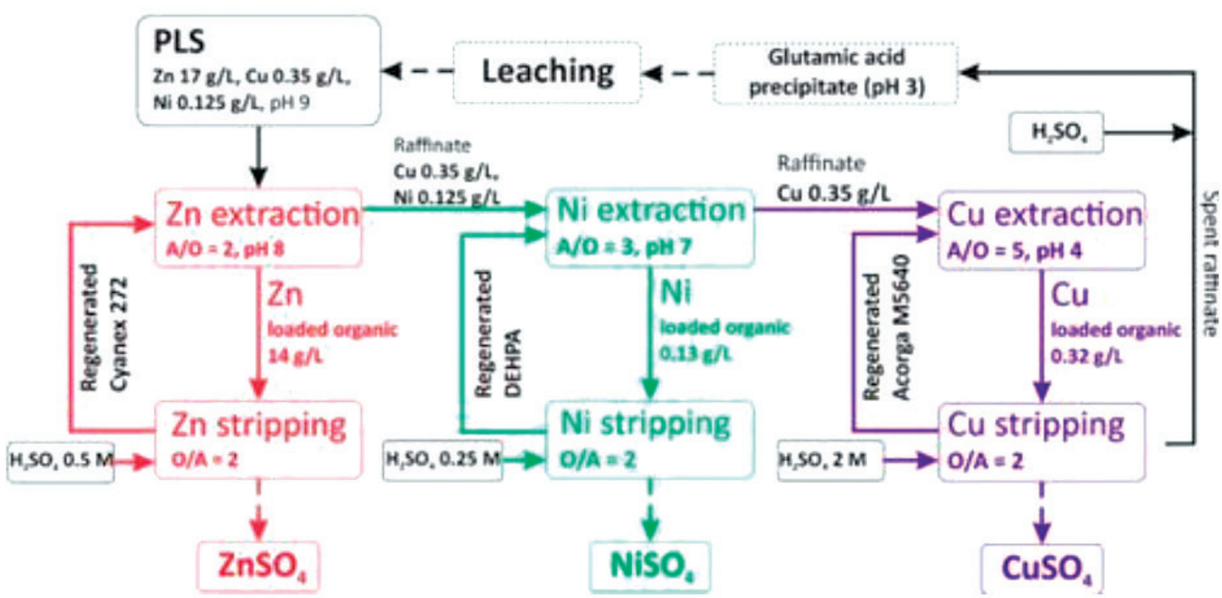

Figure 10. Species distribution diagram for glutamate-H2O at 25 °C, [glut] = 0.5 M, Eh = 0.5 V (Perea et al., 2021).

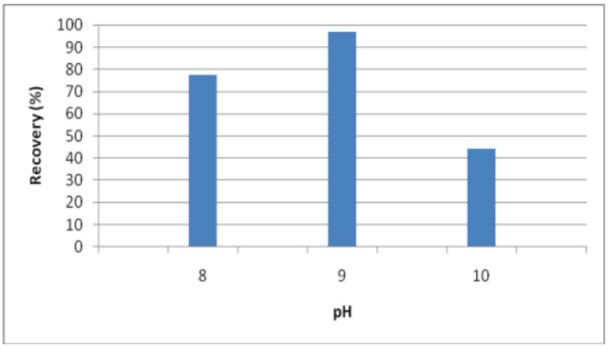

Figure 11. Effect of pH on Zn recovery (Prasetyo et al., 2021).

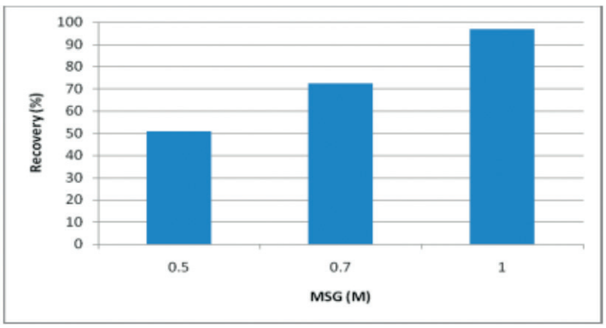

Figure 12. Effect MSG concentration on *recovery* Zn (Prasetyo et al., 2021).

12 demonstrates that MSG concentration poses positive effect on Zn leaching efficiency (Prasetyo et al., 2021).

Furthermore, there are other variables influenced the Zn recovery such as pulp density. The effect of pulp density on the recovery of Zn was examined between 15 and 25 ml/g with a constant variable of pH 9, MSG concentration of 1 M, and stirring time for 12 hours. The results (Figure 13) shows that the most optimum pulp density is 20 ml/g. Increasing the ratio between the volume of the leaching reagent and the mass of electric arc furnace (EAF) dust to higher than 20 ml/g did not significantly improve Zn recovery (Prasetyo et al., 2021).

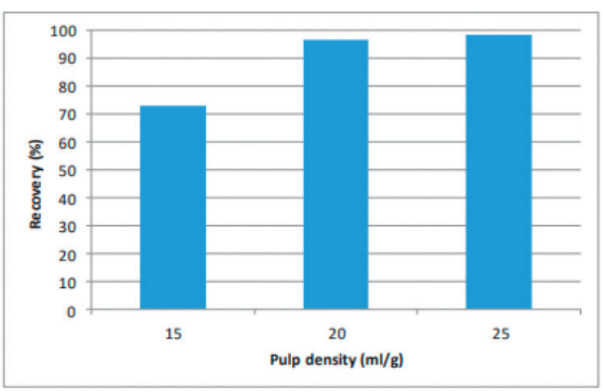

Figure 13. Effect of pulp density on Zn recovery (Prasetyo et al., 2021).

The kinetic leaching of Zn using MSG was studied at constant variables pH 9, MSG concentration of 1 M, and pulp density of 20 ml/g. It can be seen in Figure 14 that with a leaching time of up to 12 hours, the recovery of Zn increased considerably within 200 minutes, after that Zn recovery remained constant (Prasetyo et al., 2021).

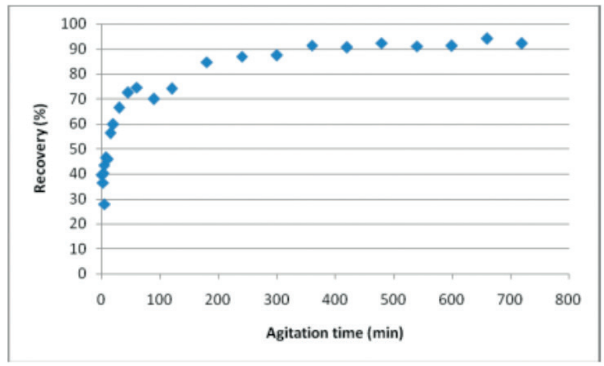

Figure 14. Effect leaching time on *recovery* Zn (Prasetyo et al., 2021).

Furthermore, based on previous research it was demonstrated that glutamate could be used as a potential cyanide substitute in alkaline electrolytes due to its ability to form complexes with bivalent metal ions (Pary et al., 2019). Based on the research, the type of oxidizing agent and its concentration can affect the kinetics of gold leaching with the highest recovery obtained using 0.03 M potassium permanganate as an oxidant at pH 9.4 (Perea and Restrepo, 2018). The strong affinity between amino acids and copper negatively affected the gold leaching process in terms of kinetic. The leaching kinetic of glycine-permanganate system was slower compared to the conventional acidic cyanide leaching system. The leaching kinetics was strongly influenced by temperature, which indicates the mechanism reactions was chemically controlled (Perea and Restrepo, 2018). Figure 15 shows the effect of temperature on Au extraction using 0.1 M glycine at temperatures of 23, 30, 40, 60, and 75°C, which hydrogen peroxide was used as oxidant. It was clear that the release of gold was strongly affected by increasing temperature.

UV-Vis spectrophotometric studies to determine the spectra of Fe(III)-glutamate complex was carried out using standard solution containing 500 g/ml iron and 1.6% glutamate in the final solution, buffered using NaCl/HCl to pH 2 (Prasetyo, 2018). Absorbance measurements were carried out within the range of 340-810 nm.

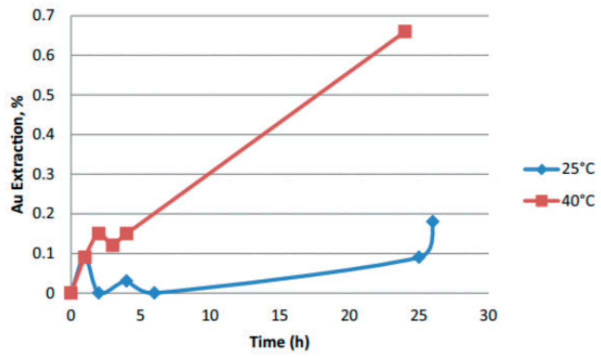

Figure 15. Effect of solution type on gold recovery rate: [Gly]= 0.5 M, [Glu]=0.5, [KMnO4]=0.01 M, pH 11 (Perea and Restrepo, 2018).

The correlation between wavelength and absorbance (absorption spectra) of the Fe(III)-glutamate complex is shown in Figure 16, which the maximum absorbance occurs at 340 nm (Prasetyo, 2018).

The level of acidity greatly affects the formation of complexes and their stability. Qualitatively, Fe(III) ions will precipitate as hydroxide at pH > 3, which is indicated by solution turbidity. At a pH less than 2.5 the color intensity fades as the Iron(III)-glutamate breaks due to the protonation of glutamate. In this case, pH 2 was chosen to avoid precipitation of Fe(III) ions and an excess glutamate was added to ensure maximum color intensity (Dunn, 2007). It can be said that MSG can be used as an alternative chromogenic reagent in the photometric determination of Fe(III) with preconcentration and dilution can be carried out according to the concentration range of 1.6-80 g/ml with a detection limit of 1.47 g/ml.

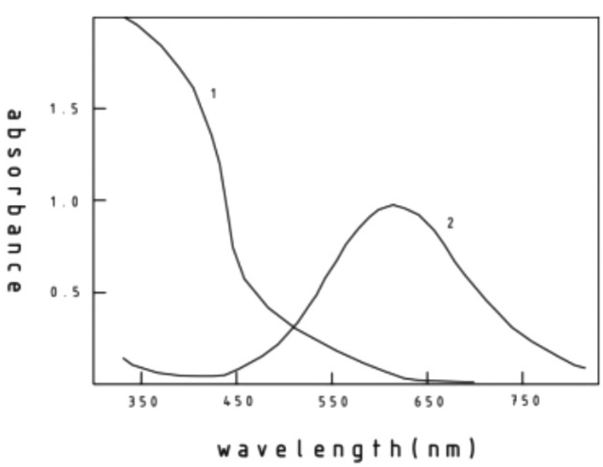

Figure 16. Absorption spectra of (1) Fe(III)-glutamate complex, Fe(III) concentration 500 g/ml, pH 2, MSG 1.6% (2) Cu-glutamate complex, Cu concentration 200 g/ml, pH 10, MSG 1.6% (Prasetyo, 2018).

The proposed method is technically simple, quantitative, easy to obtain, economical, and environmentally friendly (Marczenko and Balcerzak, 2002). Based on Table 2, the proposed photometric method using monosodium glutamate (MSG) as a chromogenic reagent to determine Fe in 5 samples yielded accuracies between 90.32% - 103.72%. In this case the results using AAS was set as the actual value. This result is even better than the standard photometric method for Fe determination such as phenanthroline method. In this case the accuracies vary between 88.70% - 106.83% compared to the AAS results (Gos and Andreas, 2015; Abdel et al., 2015).

Table 2. Determination of Fe (III) in soil samples from photometric yield and AAS in g/ml, recovery in % (photometric yield ratio/AAS). MSG and phen and standard method 1:10 each phenanthroline [17].

No	Sample	Photometric		AAS	Accuracy	
		MSG	phen		MSG	phen
1	ER/011/SL	6.85	6.93	6.71	102.2	103.4
2	ER/015/SL	5.85	6.03	6.21	94.3	97.1
3	ER/022/SL	7.09	6.96	7.85	90.3	88.7
4	ER/040/SL	5.62	5.52	6.11	91.9	90.3
5	ER/054/SL	6.56	6.76	6.32	103.7	106.8

RECENT DEVELOPMENT IN METAL EXTRACTION STUDIES USING MSG AS LEACHING REAGENT

Based on literature survey, MSG is still a new thing in the metal extraction process especially in the leaching process. The potency of MSG as leaching reagent was initially realized during the study of UV-Vis photometric analysis of iron and copper (Prasetyo, 2012). MSG can be used as an alternative chromogenic reagent in the photometric determination of Fe(III) within the range of 1.6-80 g/ml and a detection limit of 1.47 g/ml. The proposed photometry using MSG in Fe(III) determination is technically simple, quantitative, easy to obtain, economical, and environmentally friendly (Dunn, 2007). The ability of amino acid to form complex with copper negatively affects the gold leaching process in terms of leaching kinetic, which was slower compared to acidic cyanide leaching system. The study also showed that leaching kinetic was strongly influenced by temperature. This indicates that reaction mechanism was chemically controlled (Marczenko and Balcerzak, 2002). Recently, MSG has been used for leaching for Zn, Cu, and Ni from secondary source i.e. electric arc furnace dust and solvent extraction has been performed to isolate those elements from the glutamate media as the leaching product (Prasetyo and Anderson, 2020; Prasetyo et al., 2020; Prasetyo et al., 2021; Prasetyo, 2012; Brunelli and Dabalà, 2015; Murphy et al., 2020; Perea et al., 2021; Pary et al., 2019; Perea and Restrepo, 2018; Prasetyo, 2018; Dunn, 2007; Marczenko and Balcerzak, 2002; Gos and Andreas, 2015; Abdel et al., 2015). However, further study demonstrates that it is possible to use MSD as an additive in the selective reduction process of hydrometallurgy. In addition, more studies are warranted to verify the applicability of MSG as an environmentally friendly chemicals in metal extraction process at industrial scale, specifically in leaching and selective reduction process.

CONCLUSION

MSG or sodium/sodium glutamate is the sodium salt of glutamic acid, which is one of the most abundant non-essential amino acids naturally occurring in nature. Its chemical formula is $C_5H_8NO_4Na\text{-}NH_2$ and has a melting point of 232 °C or 505 °K. MSG can be used for the metal extraction process, especially leaching, as a safer substitute of toxic and corrosive reagents such as mineral acids. The research on alternative greener chemical for metal extraction is warranted to reduce the negative impacts of conventional chemicals on environment. Previous studies proved that MSG is capable to extract metals such as Fe, Mg, Cu, Zn, and Ni. Further studies, however, are still required to verify the efficacy of MSG on metal extraction at larger scale, especially for leaching and selective reduction process.

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DECLARATION

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