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In the first chapter we present, *Synthesis of magnetite and her used by $AgNO_3$ remove from aqueous system*, by MÁRQUEZ-VALDEZ, Clara, SALAZAR-HERNÁNDEZ, Mercedes, ELORZA-RODRÍGUEZ, Enrique and LÓPEZ-BAEZ, Israel, with ascription in the Universidad de Guanajuato, as a second article we present, *CO_2 absorption using LIs functionalized with amino acids*, by BARBOSA-MORENO, Gabriela, OROZCO-CUERVO, Ulises de Jesús, BARBOSA-MORENO, Alfonso and MAR-OROZCO, Carlos Eusebio, with secondment in the Tecnológico Nacional de Mexico, Instituto Tecnológico de Ciudad Madero, as the following article we present, *Effect of exogenous application of L-glutamic acid on agronomic values and seed quality of maize (Zea mays L.)*, by SENDA-NÚÑEZ, Adrián Alejandro, CASTELLANOS-HERNÁNDEZ, Osvaldo Adrián, ACEVEDO-HERNÁNDEZ, Gustavo Javier and RODRÍGUEZ-SAHAGÚN, Araceli, with affiliation at the Universidad de Guadalajara, as next article we present, *Simulation of the leaf area index from thermal units of the cauliflower (Brassica oleracea var. Botrytis) crop*, by MARTINEZ-RUIZ, Antonio, SERVIN-PALESTINA, Miguel, GALVEZ-MARROQUIN, L. Antonio and RAMÍREZ-VALLE, Orlando, with affiliation at the Instituto Nacional de Investigaciones Forestales Agrícolas y Pecuarias.

Content

Article **ECORFAN Journal-Bolivia**
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Synthesis of magnetite and her used by $AgNO_3$ remove from aqueous system

Síntesis de magnetita y su uso en la remoción de $AgNO_3$ de sistemas acuosos

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Abstract

Today pollution is an important problem that must be addressed, in this sense adsorption processes are a methodology that is usually used to remove different pollutants such as anions, cations and organic compounds. There is a great diversity of adsorbents ranging from porous oxides, metallic networks and polymeric membranes; magnetite and its composites have been shown to be adsorbent materials for the removal of various contaminants. The present work shows the study of the removal of Ag(I) from aqueous systems with Fe_3O_4 synthesized from precipitation processes. The magnetite showed an adsorption capacity of 19.84 mgg-1 according to the Langmuir adsorption model, a KL of 0.143 Lmg^{-1}, the partition coefficient showed a favorable adsorption with values between 0.1-0.01 and an endothermic Gibbs free energy. of 4.8 $KJmol^{-1}$. The kinetics of adsorption is carried out using a second order system, observing a decrease in the magnitude of the rate constant (K2) with the initial concentration of Ag(I), which suggests that the adsorption process at concentrations elevated is limited by the intra-particle diffusion of the system.

Magnetite, Adsorption, $AgNO_3$

Resumen

Hoy en día la contaminación, es un problema importante que debe de atenderse, en ese sentido los procesos de adsorción son una metodología que usualmente se utiliza para remover diferentes contaminantes como aniones, cationes y compuestos orgánicos. Existe una gran diversidad de adsorbentes que van desde óxidos porosos, redes metálicas y membranas poliméricas; la magnetita y compósitos de esta, se han mostrado como materiales adsorbentes para la remoción de diversos contaminantes. El presente trabajo muestra el estudio de la remoción de Ag(I) de sistemas acuosos con Fe_3O_4 sintetizada a partir de procesos de precipitación. La magnetita mostró una capacidad de adsorción de 19.84 mgg^{-1} de acuerdo con el modelo de adsorción de Langmuir, una K_L de 0.143 Lmg^{-1}, el coeficiente de reparto mostró una adsorción favorable con valores entre 0.1-0.01 y una energía libre de Gibbs endotérmica de 4.8 $KJmol^{-1}$. La cinética de adsorción se lleva a cabo mediante un sistema de segundo orden, observándose una disminución de la magnitud de la constante de velocidad (K_2) con la concentración inicial de la Ag(I), lo que sugiere que el proceso de adsorción a concentraciones elevadas es limitada por la difusión intra-particular del sistema.

Magnetita, Remoción, $AgNO_3$

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† Researcher contributing first author.

Introduction

Adsorption processes have been shown to be a good alternative for the removal of various contaminants in aqueous systems (metals, drugs, dyes, pesticides and others). This process has great advantages such as its simplicity, since they basically consist of placing the adsorbent with the aqueous system to be treated, either in bulk or in column [1,2], in addition to a wide range of adsorbents, such as polymeric membranes, mesoporous silica, metal oxides, MOFs, among others.

In this sense, the use of magnetite in various processes of adsorption of contaminants in aqueous systems has been published, for example Uranium (VI), Chunhui Luo et al. reported that the metal removal capacity improves with the presence of metal-reducing bacteria, associating the removal of uranium to the formation of FeUO4 species [3], the use of this metal oxide and its composites for the removal of various contaminants such as organic matter, dyes and other heavy metals such as Ni, Pb, Cd and Cr among others, both in aqueous systems and in soil, have also been reported [4-9].

The present work shows the study of the removal of Ag(I) in aqueous systems with magnetite synthesized by precipitation and hydrothermal treatment, the adsorption of the metal is evaluated using the Langmuir adsorption model, the effect of pH on the adsorption of the metal and the kinetics of adsorption of the same.

Experimental Section

Synthesis and characterization of Fe3O4

The synthesis of magnetite was carried out by precipitation techniques according to equation 1, with a 2Fe3+:Fe2+ ratio [10,11]. In a 250 mL flask, 5.27 g of FeSO4 and 2.7 g of FeCl3 were dissolved in 200 mL of water under constant stirring, then the pH was adjusted to 10-11 with NH4OH and the system was placed at reflux for 24 h. At the end of this time, the magnetite was recovered by filtration and dried at 75°C for 12 h [10,11].

$$2FeCl_3 + FeSO_4 + 8\,NH_4OH \longrightarrow Fe_3O_4 + (NH_4)_2SO_4 + 6\,NH_4Cl + 4\,H_2O$$

Reaction 1

The magnetite was characterized by powder XRD, which was carried out on a RIGAKU ULTIMA IV X-ray diffractometer.

Adsorption studies of Ag(I) from aqueous systems

The evaluation of silver(I) adsorption capacity was performed by determining the adsorption kinetics at 10 min intervals for 1 h with standard solutions of AgNO3 at different concentrations (100-500 ppm). 0.1 g of the material was placed with 10 mL of a solution at 57, 123, 192, 319 and 694 mgL-1 of Ag and the residual concentration of silver in the solution was determined at the aforementioned times by atomic absorption spectrometry.

The adsorption capacity of silver was determined by equation 1, where qt is the loading at time t, Co and Ct are the concentrations of silver in the initial solution and at time t in mgL-1, V the volume of sample used (L) and m the mass of material used in g.

$$q_t = \frac{(C_o - C_t)\,V}{m} \tag{1}$$

Effect of pH on Ag (I) Adsorption

The effect of pH on the adsorption capacity of magnetite was evaluated by determining the adsorption capacity of magnetite at pH 3, 4.5, 6 and 10. 0.1 g of the material was placed with 10 mL of Ag(I) solution at the pH under study for 20 minutes and the concentration of residual Ag in the solution was determined.

Results and discussion

Figure 1 shows the diffractogram of the synthesized magnetite, corroborating the obtaining of this phase. The planes are observed at 2□ at 30.1, 35.4, 43.1, 54.5, 57.6, 62º, which correspond to the magnetite according to Mohammadi et al].

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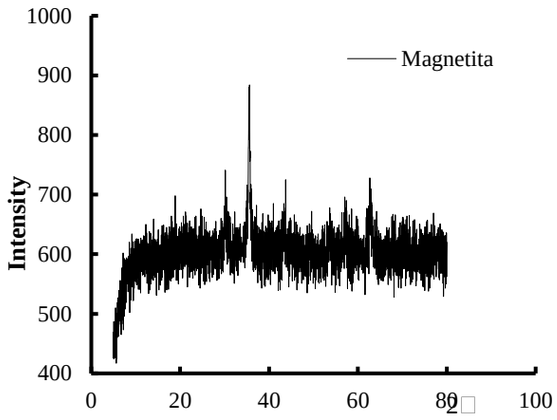
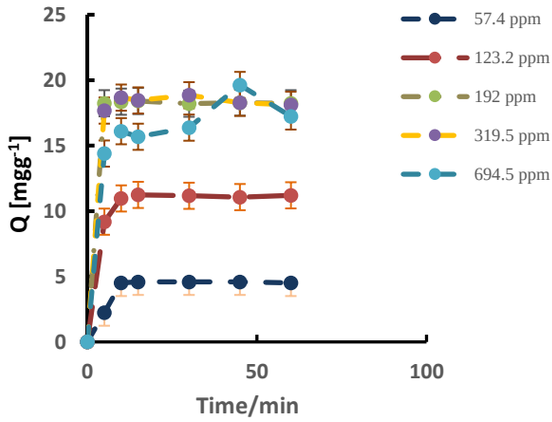


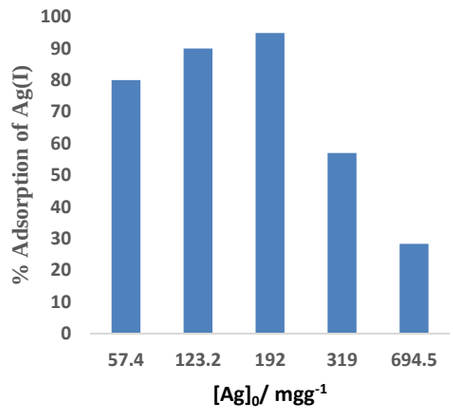
Graphic 1 XRD Synthesized magnetite

Adsorption studies of Ag(I) from aqueous systems

Figure 2 shows the adsorption isotherms of Ag(I) with the synthesized Fe_3O_4, observing an adsorption equilibrium after 20 minutes of contact. A removal of 80 to 95% was observed at moderate concentrations of 57 to 200 mgL^{-1} Ag, decreasing to 28% at high concentrations of 700 mgL-1 Ag (Figure 3).



Graphic 2 Adsorption isotherms of Ag(I) with Fe_3O_4



Graphic 3 Adsorption capacity of Ag(I) with Fe_3O_4

The fit of the experimental data to the Langmuir and Freundlich adsorption models showed a poor fit to the Freundlich model (Figure 4b), fitting the experimental data only to the Langmuir model (Equation 2, Figure 4a), where Ce and qe refer to the concentration and charge at equilibrium of the system, KL represents the Langmuir constant and Q0 the maximum charge for the formation of the monolayer. This model assumes that adsorbate-adsorbate interactions are weak (physisorption) and that there are no adsorbate-adsorbate interactions [13, 14].

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_0} + \frac{C_e}{Q_0} \quad (2)$$

Figure 4a, shows the fit of the experimental data to the Langmuir model, showing a maximum loading capacity (Q0) of 19.84 mgg-1 of Ag(I) and a Langmuir constant (KL) of 0.143 Lmg^{-1}. The Gibbs free energy was determined from Equation 3, where R is the gas constant (8.314 JK^{-1} mol^{-1}), T the absolute temperature and KL the Langmuir constant; an endothermic adsorption process was observed with a magnitude of 4.8 $KJmol^{-1}$. The partition coefficient (RL), was determined according to Equation 4, where KL is the Langmuir constant and C0 the initial concentration of sorbate (Ag(I)); the magnitude of RL, is a parameter that allows identifying if the adsorption process is favorable or not; when the system presents values of RL=1, the adsorption process is linear, while values of RL=0 imply an irreversible adsorption process and for values of 0<RL<1, the adsorption process is favorable. The adsorption system of Ag(I) on Fe_3O_4, showed RL magnitudes in the range of 0.1-0.01, suggesting a favorable adsorption process.

$$\Delta G = -RTlnK_L \quad (3)$$

$$R_L = \frac{1}{1+K_L C_0} \quad (4)$$

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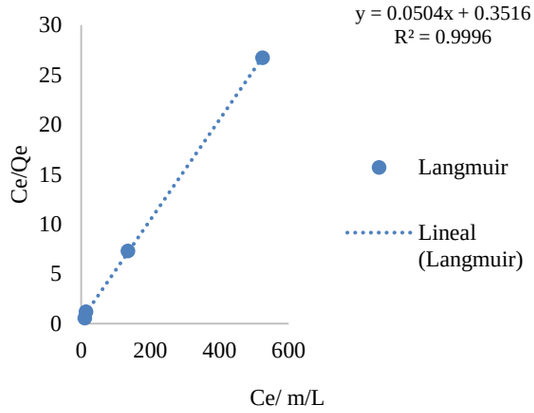
(a)



(b)

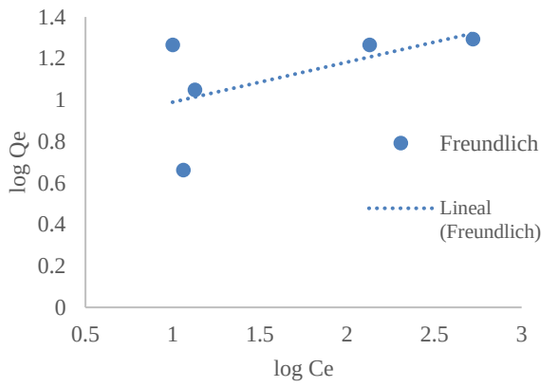


Figure 4 Fit of experimental data to the model of (a) Langmuir and (b) Freundlich.

The adsorption kinetics was adjusted to the pseudo-second order model (Equation 5 and 6), where qe and qt, are the charges at equilibrium and at time t and K2 the velocity constant of the system. The velocity constant of the system, values from 0.22 to 0.057 gmg-1min-1 were observed. The rate constant decreases as the initial Ag(I) concentration of the system increases (Figure 5), suggesting that at high concentrations the adsorption mechanism is limited by intraparticle diffusion [13, 14].

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \quad (5)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

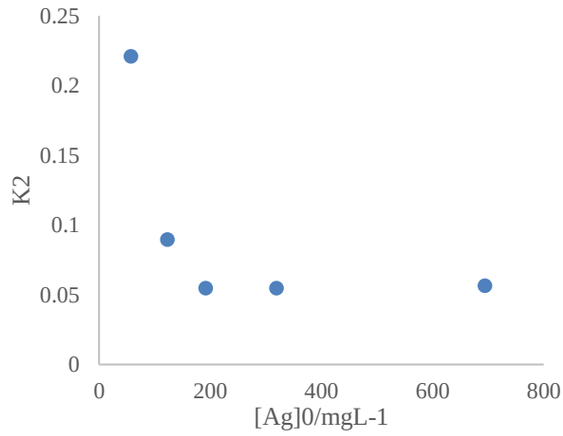


Figure 5 Dependence of K_2 on the initial Ag(I) concentratio

Effect of pH on the adsorption of Ag(I) from aqueous systems with Fe_3O_4

Figure 6 shows the effect of pH on the adsorption of $[Ag(H_2O)_2]+$ with magnetite, a decrease in the adsorption capacity of the material is observed as the pH of the system increases, with 78% removal at acidic pH (3) and decreasing as the pH increases in the system, with only 51% removal at pH 6.0. This decrease is due to the change of the magnetite surface charge at pH higher than 3.0, which disfavors the Fe-Ag interactions and the adsorption process, at basic pH (3.0).

At basic pH (10), the quantitative removal of silver from the system is observed, this is due to the precipitation of Ag (OH) (Kps= 1.5X10-8), which favors the removal of the metal by precipitation and not adsorption processes.

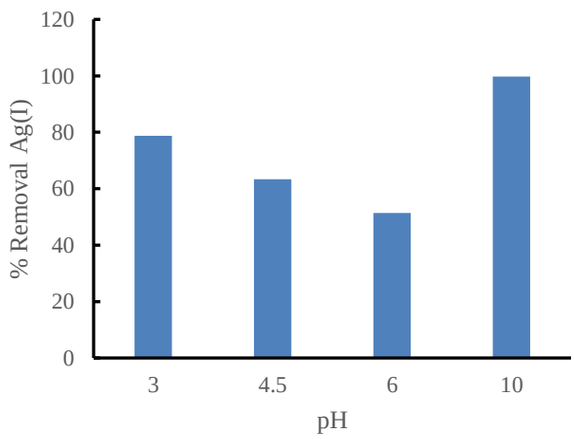


Figure 6 Effect of pH on the adsorption process of Ag(I)

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Conclusions

The removal of Ag(I) in aqueous systems with Fe_3O_4, is favorable at acidic pH <3, where the highest metal removal is observed at 78 %. The removal capacity of silver with magnetite is moderate, according to the Langmuir model, the maximum loading capacity for the formation of the monolayer on the surface is 19.84 mgg^{-1}, the KL is 0.143 Lmg^{-1}. The adsorption kinetics is carried out by a second pseudo-order model, the rate constant decreases with respect to the initial concentration of silver in the system, suggesting that intra-particle diffusion governs the adsorption process at high concentrations, while external diffusion is the main resistance at low concentrations.

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CO_2 absorption using LIs functionalized with amino acids

Absorción de CO_2 utilizando LIs funcionalizados con aminoácidos

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Abstract

A comparative study was conducted on the absorption of carbon dioxide (CO_2) using ionic liquids (ILs) based on imidazole derivatives as cations and amino acids as anions ([BMI][AA] and [OMI][AA]). The synthesized ILs were characterized using Fourier Transform Infrared Spectroscopy, and absorption studies were conducted using a pressurized batch system under stable pressure and temperature conditions. Amino acids demonstrated an enhancement in the absorption of this acidic gas when compared to monoethanolamine, which is the most commonly used commercial absorbent compound.

Absorption, Ionic Liquids, CO_2

Resumen

Se realizó un estudio comparativo de la absorción de dióxido de carbono (CO_2) utilizando líquidos iónicos (LIs) basados en derivados de imidazol como cationes y aminoácidos como aniones ([BMI][AA] y [OMI][AA]). Los LIs sintetizados fueron caracterizados por espectroscopia infrarroja por Transformada de Fourier y los estudios de absorción se realizaron mediante un sistema de lotes presurizado a condiciones de presión y temperatura estables. Los aminoácidos mostraron una mejora en la absorción de este gas acido comparados con la monoetanolamina que es el compuesto absorbente comercial mas utilizado.

Absorción, Líquidos iónicos, CO_2

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Introduction

The main source of energy worldwide has been from non-renewable compounds which, when used, generate some acid gases, CO_2 being the one with the highest concentration and contributing to a large extent to the greenhouse effect. The production of this gas is not only increased by the above but also by other factors such as the burning of coal in power plants or those plants based on diesel, which are very frequent and harmful emission sources [1,2]. The economic development of countries, especially those in the process of growth, is linked to an increase in the demand for energy; therefore, projections indicate that the need for fossil fuels will continue to increase given the trend of a growing world population that demands more and more energy per inhabitant, making it increasingly necessary to develop new efficient and low-cost environmental technologies [3].

Among the main options for reducing CO_2 emissions are improving the efficiency of conventional power plants, having greater control over energy consumption, using a higher proportion of renewable resources, developing nuclear energy sources, and capturing and storing CO_2, the latter being the most feasible and possible option to develop at present, which is why it has assumed an important role in the last century [4-6].

Nature has its own method for capturing CO_2 using trees, resulting in its biological fixation; however, experts are more curious about developing new non-biological processes for CO_2 capture in large point sources, so several viable options for achieving this involving different processes are presented [7] Post-combustion, oxy-combustion and pre-combustion are the three main technological routes that are currently considered in CO_2 capture [8,9]. One of the advantages of post-combustion capture is that because capture occurs after combustion and before release to the atmosphere, it can be implemented in facilities that are still in operation [10].

Absorption is considered within this capture stage, in this process chemical solvents implement an acid-base chemical reaction and among the best known are alkane amines (generally called amines). Primary amines are more reactive with CO_2 but are also more corrosive and sensitive to degradation, so secondary and tertiary amines are used to reduce these characteristics [11-13].

LIs commonly known as "green solvents" have been noted as promising candidates for CO_2 adsorption removal due to their high thermal stability, negligible vapour pressure and adjustable physicochemical properties [14-20]. LIs exhibit a strong affinity to CO_2 that are derived by varying the cations or anions by the addition of functional groups, especially those containing amino groups [21-24]. The anion plays a key role in determining the solubility of CO_2 in LIs and by physically adsorbing CO_2, less energy is needed for the regeneration of LIs [25]. Therefore, it has been deduced that anions in conventional ILs have a greater impact on CO_2 solubility than cations [26-29]. It has been proven that when functionalised LIs are dissolved they can greatly reduce viscosity [30]. The adsorption capacity of most existing functionalised LIs solutions with a single functional group has been similarly reported for compounds with approximately 0.5 mol CO_2/mol LIs [31-33].

Therefore, in order to develop new materials that can function as CO_2 absorbers, LIs were functionalised by the addition of amino acid groups to take advantage of the advantages of LIs by improving the characteristics with respect to conventional amine absorbing composites.

Methodology to be developed

Synthesis of the functionalised LIs

Amino acid functionalised LIs [OMI][AA] and [BMI][AA] were synthesised in the laboratory by replacement and neutralisation reactions using Lysine [L], Arginine [A], Histidine [H] and Glutamine [G] as amino acids. The synthesis of the precursor LIs [R-MI][Br] starts with the alkylation of 1-methylimidazolium (0.1 mol) with the corresponding alkyl halide (0.11 mol) in an inert atmosphere for 48 hours with heating and magnetic stirring.

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The anion exchange reaction was performed based on the metathesis of halide salts with potassium hydroxide (KOH) in ethanol at low temperatures (below 10°C) in an equimolar fashion to form the precursor LI [R-MI][OH], which was subsequently filtered to remove excess salt in the sample and neutralised with the corresponding AA under constant stirring at room temperature. The ethanol was then distilled under vacuum to remove it from the [R-MI][AA] solutions before use. The proposed reaction mechanism can be seen in figure 1. The nomenclature used throughout this study is presented in table 1.

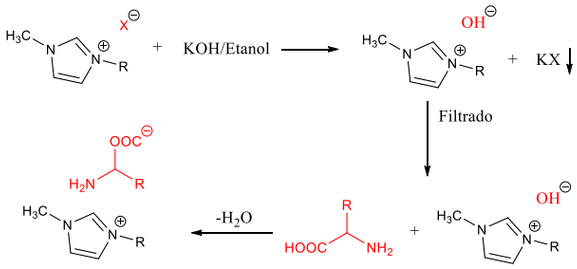

Figure 1 Reaction scheme for the synthesis of LIs functionalised with amino acids

No.	Cation	Anion	Identification
1	1- Butil, 3-Metilimidazol	Lysine	[BMI][L]
2		Arginine	[BMI][A]
3		Glutamine	[BMI][G]
4		Histidine	[BMI][H]
5	1-Metil, 3-Octilimidazol	Lysine	[OMI][L]
6		Arginine	[OMI][A]
7		Glutamine	[OMI][G]
8		Histidine	[OMI][H]

Table 1. Amino acid-functionalised ILs in this study

CO_2 absorption with LIs-Aas

The absorption tests were carried out at 303 K and a pressure of 3 atm. The apparatus consists of a stainless steel gas tank under constant stirring with a digital manometer connected, the diagram is shown in figure 1. The temperature is controlled by a thermostat in the heating bath (± 0.1 K variation). The variation in gas pressure was approximately ±0.001 bar over the pressure range used. Approximately 10 g of pure [R-MI][AA] or dissolved in water was measured into the reservoir and hermetically sealed. The first step consists of removing the air in the system by means of a vacuum pump to which it is connected for about 15 minutes. Subsequently the CO_2 is loaded into the tank and starts the absorption process with agitation. The system is considered as an equilibrium state once the pressure remains constant.

The concentration of absorbed CO_2 is determined using the ideal gas equation of state due to the pressure conditions handled. The variation in the absorption measurement results is approximately 0.02 mol CO_2/ mol LI.

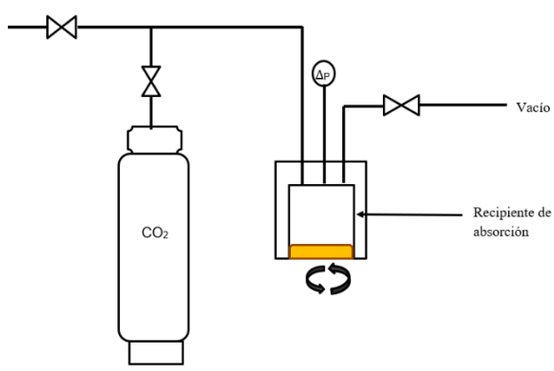

Figure 2 Schematic of the absorption equipment used

Figure 2 shows a very marked signal concerning the ionic liquid [BMIM+] centred at 3378 cm^{-1} which is attributed to the quaternary ammonium salt formed with the halogen (-N+R4X-), the formation of this band is due to the hydrogen bridge interaction formed between the acid hydrogen of the imidazole ring and the halogen ion, which weakens the C-H bond and decreases the location frequency resulting in an increase in signal intensity and a broadening of the band [34].

The next band is observed in all LIs functionalised with AAs, between 3500-3100 cm-1, this signal is attributed to the -NH groups and becomes broader because it overlaps with the -OH stretch in the amino acid structure [35]. The bands located at 3200-3000 cm^{-1} and 1166 cm-1 correspond to the vibrational modes of the imidazole ring, symmetric and asymmetric stretches of the C-C, N=C, C=C and N-C groups [36]. In LIs-AAs, at 1590 cm-1 a pronounced stretching is observed and at 1376 cm^{-1} a weaker one attributed to the C=O group of the ("CO_2") [37]. At 1660 cm^{-1} and between 1550-1300 cm-1 asymmetric bending bands of NH^{3+} are present [37] When comparing the spectrum of [BMIM+] with the [BMIM+][AA-] the differences are remarkable, which confirm the functionalisation of the precursor LI with the AAs, since the appearance of the characteristic band of the imidazole ring resonance near 3000 cm^{-1} is detected, which continues to be present even with the incorporation of these compounds.

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It is also possible to observe that the compound with a linear anion and with a large amount of NH_2 groups such as lysine, has a good absorbance due to the fact that these groups are less attracted to other electronegative elements, which allows a greater dispersion of the anions and a better interaction between them. [38].

Results

Characterisation

The FTIR spectra of the synthesised ionic liquids are described below:

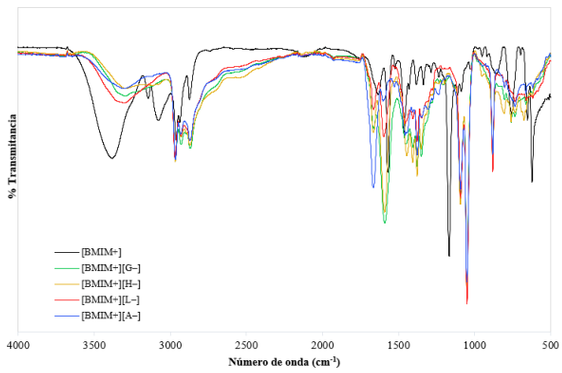

Figure 3 FTIR spectrum of the [BMIM+] [AA-] family of LIs

Figure 3 again shows a signal for the [OMIM+] LI centred at 3398 cm-1 that is attributed to the quaternary ammonium salt formed with the halogen (-N+R4X-) [35]. The bands observed between 3500-3100 cm^{-1} are signals attributed to the -NH groups with the -OH stretch in the AA structure of LIs functionalised with the same [35]. The bands located at 3200-3000 cm^{-1} and 1166 cm^{-1} correspond to the vibrational modes of the imidazole ring, symmetric and asymmetric stretching of the C-C, N=C, C=C and N-C groups [36]. On the other hand, in LIs-AAs, at 1570 cm-1 a pronounced stretching is observed and at 1350 cm-1 a weaker one, attributed to the C=O group of the CO_2. [37]. At 1674 cm-1 and between 1550-1300 cm-1 asymmetric NH^{3+} bending bands are present [37] Comparing the spectrum of [OMIM+] with the [OMIM+][AA-] again confirms the functionalisation of the precursor LI with each AA, as the appearance of the characteristic band of the imidazole ring resonance near 3000 cm^{-1} is detected in all structures.

It is possible to observe a shift and amplitude in the signals near 3200 cm^{-1}, which is attributed to the increase of the alkyl chain present in the cation, which presents a higher number of C-H bonds and therefore increases the absorbance [38].

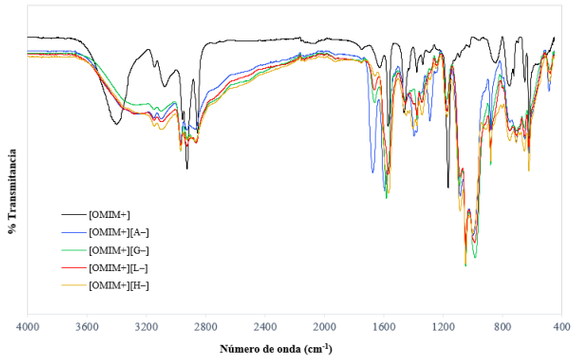

Figure 4 FTIR spectrum of the [OMIM+][AA-] family of LIs

CO_2 adsorption with ionic liquids

Solubility tests were performed on pure and dissolved LIs in water, in all cases, the absorption capacity of the LIs was higher in aqueous solution due to the fact that their viscosity is reduced when diluted. At the end of the absorption tests carried out with the LI-water solutions, especially those of [BMI][AA], a gas release was observed, which is attributed to the fact that not only chemisorption but also physisorption takes place during the absorption process. It should be noted that the solubility of the materials is more promising than with pure MEA. The absorption results can be seen in detail in table 2.

No.	Identification	(mmol CO_2/ mol LI)	
		LI puro	LI in aqueous solution (35%)
1	[BMI][L]	821.47	1109.38
2	[BMI][A]	788.58	1057.80
3	[BMI][G]	761.94	1023.85
4	[BMI][H]	748.32	1010.70
5	[OMI][L]	719.25	1298.41
6	[OMI][A]	708.47	1268.43
7	[OMI][G]	902.62	1212.20
8	[OMI][H]	891.55	1200.45
9	MEA	-----	470.54

Table 2 Absorption results of the amino acid functionalised LIs

Figure 4 presents a comparison between the adsorption capacity of MEA and functionalised LIs-AA. It can be clearly seen how CO_2 solubility is favoured with these compounds, especially with lysine anions.

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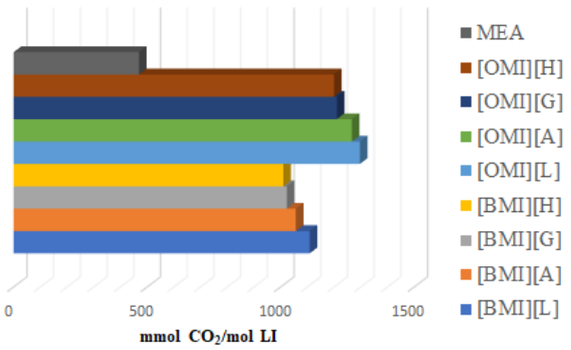

Figure 5 Absorption capacity of LIs-AA in 35% mass aqueous solution

The influence of the LIs cations on CO_2 solubility was studied with a similar anion between the butyl and octyl chains. Figure 5 shows that lysine greatly favours the absorption of CO_2, this is attributed to its solubility given its molecular structure which makes it favourable to the interaction with the gas.

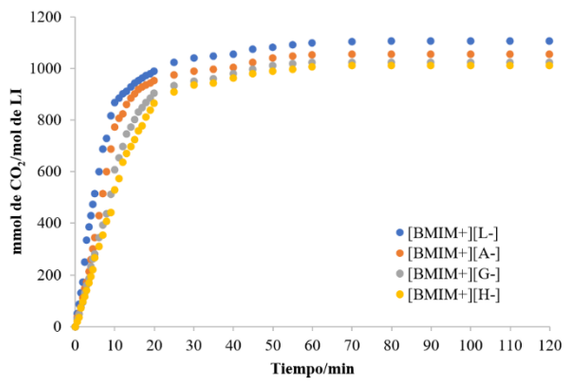

Figure 6 Variation in the absorption capacity of diluted [BMIM+][AA-]

Figure 6 shows that the absorption capacity is favoured in a similar way to that of lysine, despite the fact that the LIs with the longest alkyl chain are present in this one. A comparison between both figures shows that the absorption capacity is favoured in a similar way to the length of the chain, this can be attributed to the fact that the longer the alkyl chain, the greater the dispersion force of the cation, improving the interaction with CO_2 [39,40].

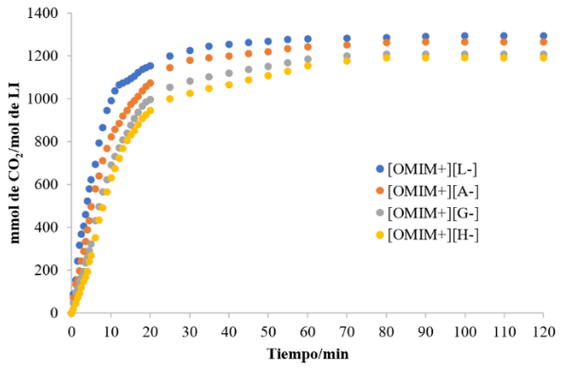

Figure 7 Variation of the absorption capacity of diluted [OMIM+][AA-]

The excellent properties of LIs and their ability to synthesise them highlight their importance in adsorption processes. In some cases it is possible to appreciate that the reaction kinetics of LIs-AA is higher compared to conventional amines. Figure 7 shows the comparative kinetics of lysine-functionalised ILs compared to MEA, and it is possible to appreciate that the reaction kinetics is faster with respect to these materials.

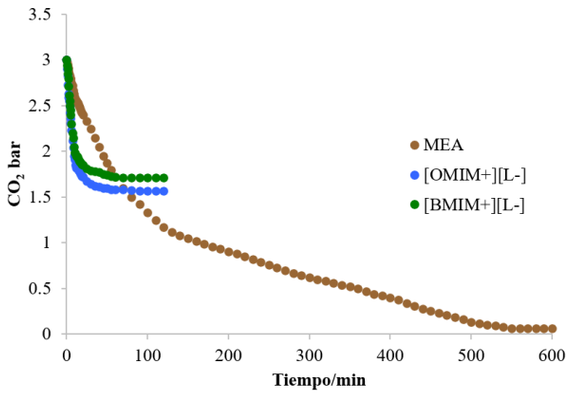

Figure 8 Absorption kinetics of lysine derivatives compared to MEA

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Conclusions

The [OMI]-derived ILs obtained the most promising results compared to [BMI]-derived ILs, because the absorption is favoured with the length of the alkyl chain, obtaining the best results with the lysine amino acid since the amount of amino groups (especially primary) in the anions as well as the structural arrangement favours the absorption.

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The solubility of CO_2 was favoured with dilution of these LIs-AA in water, which is mainly attributed to physisorption processes.

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Article **ECORFAN Journal-Bolivia**
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Effect of exogenous application of L-glutamic acid on agronomic values and seed quality of maize (*Zea mays* L.)

Efecto de la aplicación exógena de ácido L-glutámico sobre valores agronómicos y calidad de semillas de maíz (*Zea mays* L.)

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Abstract

The application of amino acids as biostimulants in agriculture has allowed for the improvement of performance parameters in a wide variety of crops. The objective of this study was to evaluate the effects of four concentrations of L-glutamic acid in mg·L-1 (L-Glu0, L-Glu200, L-Glu400, and L-Glu800) following seed treatment and foliar sprays in rainfed maize. Both agronomic and biochemical parameters were determined, and the data obtained were evaluated through analysis of variance (ANOVA) and Duncan's mean comparison test ($P \leq 0.05$). The application of L-Glu800 significantly increased chlorophyll b content, fresh weight, dry weight, grain yield, 100-seed weight, and crude fat content of the grains. L-Glu applications also increased plant height, germination rate, kernel hardness, soluble protein content, and decreased ash content in the grain.

Plant biostimulation, Amino acid, Maize

Resumen

La aplicación de aminoácidos como bioestimulates en agricultura ha permitido la mejora de parámetros de rendimiento en una amplia variedad de cultivos. El objetivo de este trabajo consistió en evaluar los efectos de cuatro concentraciones de ácido L-glutámico en mg·L-1 (L-Glu0, L-Glu200, L-Glu400 y L-Glu800) luego del tratamiento de semillas y aspersiones foliares en maíz de temporal de lluvia. Se determinaron tanto parámetros agronómicos como bioquímicos, y los datos obtenidos fueron evaluados mediante un análisis de varianza (ANOVA) y la prueba de comparación de medias de Duncan ($P \leq 0.05$). La aplicación de L-Glu800 aumentó significativamente el contenido de clorofila b, el peso fresco, el peso seco, el rendimiento de grano, el peso de 100 semillas y el contenido de grasa cruda de los granos. Las aplicaciones de L-Glu también incrementaron la altura de la planta, la tasa de germinación, la dureza y el contenido de proteína soluble de la semilla, y disminuyeron el contenido de cenizas en el grano

Bioestimulación vegetal, Aminoácido, Maíz

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Introduction

The term "biostimulant," when referring to plant nutrition, pertains to substances or microorganisms that promote plant growth, enhance tolerance to abiotic stress, and/or improve crop quality characteristics, regardless of their nutrient content (Calvo *et al.*, 2014; Du Jardin, 2015, Iqbal *et al.*, 2021). Some of these biostimulants have the capacity to influence metabolic, physiological, and morphological processes, as well as the interaction of the plant with the ecosystem (Woo and Pepe, 2018). A biostimulant can be a molecule in its pure state or complex mixtures of substances with variable compositions. According to Du Jardin (2015), substances such as humic compounds, algae and/or plant extracts, beneficial fungi and bacteria, chitosans, biopolymers, inorganic compounds, protein hydrolysates, or nitrogenous compounds like peptides and free amino acids can be included in the category of biostimulants. Particularly, the benefits of exogenous application of free amino acids in plants have been extensively studied, with a focus on supply through foliar solutions as a method of rapid absorption (Haghighi *et al*., 2022). Raposo-Junior *et al*. (2013) reported an increase in the yield of sugarcane (*Saccharum officinarum*) when a biostimulant formulation with amino acids was applied, while Al-Karakia and Othman (2023) found that amino acid application influences biomass increase in lettuce (*Lactuca sativa*). In the same species, Noroozlo *et al.* (2019) increased vitamin and mineral content through foliar sprays with glycine and glutamine. In tomato (*Solanum lycopersicum*), the application of tyrosine, lysine, and methionine has the capacity to raise sugar content (Alfosea-Simón *et al*., 2020).

L-Glutamic acid (L-Glu) is an essential amino acid that plays various roles in plants. Beyond protein synthesis, in its free form it acts as a chelating agent, growth stimulator, and inducer of resistance to biotic and abiotic stress. It also serves as an organic nitrogen reservoir for the synthesis of other amino acids such as proline and γ-aminobutyric acid (GABA). Additionally, it functions as an inhibitor of abscisic acid in seed germination (Kong *et al*., 2015; Qiu *et al.*, 2020). L-Glu acts as a signaling molecule in stress situations (Toyota *et al.*, 2018) and can restore beneficial microbiota in flowers and the rhizosphere (Kim *et al.*, 2021).

Furthermore, foliar application of L-Glu can increase oil levels, proline content (Ahmed *et al.*, 2017), stimulate growth (Soares *et al.*, 2016), induce resistance to pathogens (Goto *et al.*, 2020), and enhance biomass, photosynthetic pigment content, protein, and nitrogen levels (Yu *et al.*, 2010).

Maize (*Zea mays*) is one of the most significant crops globally in terms of production volume and one of the crucial grains for human consumption on an international scale (Ureta *et al.*, 2020). The fruits can be harvested in their tender state for consumption as a vegetable, while the dried grain is used for direct human consumption or as a raw material for the production of oils, syrups, alcoholic beverages, and biofuels (Cooter *et al.*, 2017) (Figure 1).

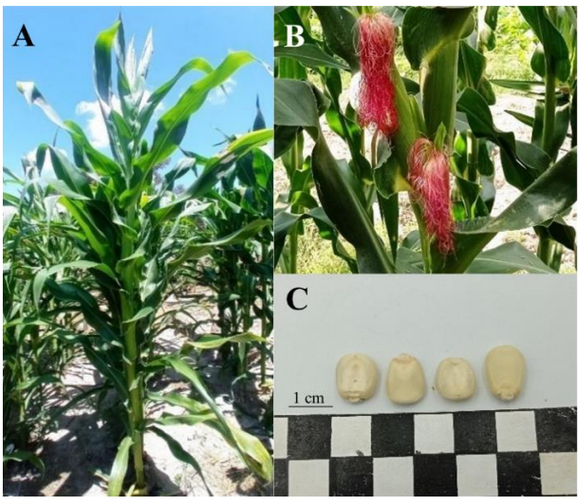

Figure 1 Zea. *mays*: A. plant; B. ears and C. dry kernels

A s Mexico is the center of origin and diversification of maize (Kato *et al.*, 2009), it stands as one of the largest repositories of genetic diversity worldwide, harboring approximately 50% of the known diversity in the American continent. Furthermore, maize is a staple food in Mexico, constituting over 50% of the caloric intake in many population sectors (SADER, 2021). This country is the eighth-largest maize producer globally, generating around 27.5 million tons of grain and 17.25 million tons of forage in the year 2021. Sinaloa, Jalisco, and the State of Mexico are the leading entities in maize production in the country (SIAP, 2022).

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While the benefits of L-Glu on phytochemical content and plant growth under stress conditions have been extensively studied, there is less information regarding its effects on cereal yield. The objective of the present study was to assess the effects of different concentrations of L-glutamic acid on the production of white maize under rainfed conditions.

Materials and Methods

Field Conditions

The trials were conducted under rainfed or seasonal rain conditions between June and November 2022 in the locality of Zalamea, La Barca municipality, Jalisco, Mexico, located at coordinates 20°18'42.6"N 102°30'29.7"W, at an altitude of 1533 meters above sea level. Prior to sowing, a soil chemical analysis was performed (Table 1) using the methods for the HI83325 multiparameter photometer (HANNA®). Specifically, the following reagents were employed: HI93715-03 (ammonium nitrogen), HI93717-01 (phosphate), HI93750-01 (potassium), HI937521-01 (calcium), HI937520-01 (magnesium), and HI937501-0 (sulfate). The pH was determined using a Bante920 Benchtop pH Meter (Bante Instruments®).

Concentration in parts per million (ppm)						
pH	N (NH_3)	K (K_2O)	P (PO_4^{3-})	Ca (Ca^{2+})	Mg (Mg^{2+})	S (SO_4^{2-})
6.8	0.49	22	3.05	112.5	8.5	29
6.0-7.2*	25-40**	131-175**	36-50**	>400**	>30**	>10**
*Desirable pH range for mineral soils; **Optimal ranges of nutrient concentrations (Espinoza et al., 2012; MSU, 2023).						

Table 1 Chemical soil characteristics prior to maize sowing

Inorganic fertilization with a triple 17 physical mixture (N-P-K) was applied during sowing, followed by two subsequent fertilizations using urea after the crops were established. Seed sowing was done manually on June 12th and 13th, 2022, in rows oriented from east to west, placing 9 seeds per linear meter at a depth of 5 cm and with a spacing of 75 cm between rows. To manage pests, tefluthrin was employed against the fall armyworm (*Helicoverpa armigera*) and blind chicken (*Phyllophaga* spp.).

Experimental design

The design was completely randomized with one single factor and three replications per treatment, with experimental units consisting of rows of 10 plants.

Seed treatment

Commercial white maize seeds were obtained from a local market, selecting those with healthy and uniform morphology. The seeds were subjected to a triple wash with sterile distilled water and then immersed for 1 hour in 10 mL of aqueous solutions of L-glutamic acid (Sigma-Aldrich®) at three concentrations: 200 $mg \cdot L^{-1}$, 400 $mg \cdot L^{-1}$, and 800 $mg \cdot L^{-1}$, along with a control or reference treatment (L-Glu0).

Foliar sprays

The first application of L-Glu took place 30 days after sowing (DAS) when most of the plants were in the V6-V7 stages, using a manual sprayer until reaching the dew point. The same solutions used during pre-sowing (L-Glu0, L-Glu200, L-Glu400, and L-Glu800) were applied. The second spray was conducted at 60 DAS, coinciding with the appearance of the flag leaf (stages V12-V14). These applications were carried out between 8-9 A.M.

Agronomic parameters

Plant height

The height of the plants was determined at 100 DAS, using a measuring tape. For this parameter, only the aboveground part was measured, from the root collar to the tip of the panicle (cm).

Plant weight

Fresh weight was assessed by randomly selecting three plants per treatment at 100 DAS, including their roots. The soil was carefully removed with running water, and the plants were then weighed using a digital scale (Torrey L-PRC®). For dry weight measurement, the plants were dried in partial shade for two weeks before being re-evaluated on the scale. Measurements were expressed in kilograms (kg).

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Ear size

At 140 DAS, ears from each treatment were harvested, and their length and diameter were measured (cm) using a measuring tape.

Grain Yield per Plant

The harvested ears were placed in partial shade at room temperature for two weeks to reduce moisture content. Kernels of each ear were manually removed, and their total weight was determined in grams (g) using a precision analytical balance (A&D Company, Limited®).

Weight of 100 Seeds

This test involves randomly selecting and weighing 100 seeds per treatment, aiding in the estimation of seed size according to the methodology proposed by Palacios Rojas (2018). One hundred seeds were randomly chosen, and their combined weight was determined in grams (g).

Seed flotation index

Flotation index is an indirect parameter of grain hardness. The test was conducted in accordance with the specifications of Mexican Standard NMX-FF-034/1-SCFI-2002, wherein the seeds undergo flotation in a solution with a specific density (ρ) of 1.25 $g \cdot mL^{-1}$. One hundred seeds in good physical condition were selected, immersed in 500 mL of a 67% sucrose solution, stirred with a stainless-steel spatula, and allowed to rest for 1 minute (Palacios Rojas, 2018). The floating seeds were removed from the solution and counted. The flotation index was determined using the following formula:

$$Flotationindex = \frac{Floatingseeds}{Totalseeds} * 100 \quad (1)$$

Seed germination rate

Germination tests were conducted based on the methodologies proposed by Akinyosoye *et al*. (2014) and Odje *et al*. (2022) with some modifications. The seeds underwent a wash with running water and sodium dodecyl sulfate (SDS) as a detergent, followed by disinfection in 70% ethanol for 3 minutes, then immersion in a 50% commercial solution of sodium hypochlorite (NaClO) for 5 minutes, and were rinsed three times with sterile distilled water.

Finally, the seeds were germinated on autoclave-sterilized paper towels (121 °C/15 psi/15 min), moistened with sterile running water. Twenty seeds were placed on each paper towel, wrapped in transparent plastic bags, and kept in semi-darkness for germination over 7 days. Germination rate was determined using the following formula:

$$Germinationrate = \frac{Germinatedseeds}{Totalseeds} * 100 \quad (2)$$

Seedling size

Randomly selected maize seedlings from the germination test at 7 DAS were measured using a millimeter ruler, evaluating the total length of the shoot, cotyledon, and primary root in centimeters (cm).

Biochemical parameters

Photosynthetic pigments

The extraction of photosynthetic pigments was carried out following the 80% acetone method described by Ghosh *et al*. (2018) with some modifications. One hundred milligrams of fresh leaves were taken and macerated in a cold mortar with 5 mL of 80% acetone previously cooled to 4°C. Subsequently, the mixture was centrifuged at 8,000 rpm for 8 minutes, and the supernatant was poured into Falcon tubes, repeating this step until the tissue was depleted, and the supernatant became colorless. The volume was brought up to 15 mL. The absorbance of the extract was measured at 470 nm, 645 nm, and 663 nm against the solvent as a blank using a UV-Vis spectrophotometer GENESYS™ 150. Arnon's equations (1949) were used for quantifying chlorophyll a, b, and total chlorophyll, while Lichtenthaler and Wellburn's equation (1983) was employed to estimate total carotenoids in milligrams per gram of fresh tissue ($mg \cdot gft^{-1}$):

$$Cla = \frac{12.7(A663) - 2.69(A645) * V}{1000 * W} \quad (3)$$

$$Clb = \frac{22.9(A645) - 4.69(A645) * V}{1000 * W} \quad (4)$$

$$Clt = \frac{20.9(A645) + 8.02(A663) * V}{1000 * W} \quad (5)$$

$$Ctd = \frac{1000(A470) - 1.82(Cla) - 82.02(Clb)}{198} \quad (6)$$

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Where:

Cla: Chlorophyll a

Clb: Chlorophyll b

Clt: Total chlorophylls

Ctd: Total carotenoids

A: Absorbance for the given wavelength

V: Final volume of chlorophyll extract in 80% acetone (mL)

W: Fresh weight of the tissue (g)

Ash content

The method 08-01 (AACC, 1995) was employed for the quantification of total ash. Whole grain flour was obtained from 10 g of harvested maize seeds, which underwent grinding using a mill (Hamilton Beach® 80393). Porcelain crucibles were used and placed in an electric muffle furnace (Terlab™) at 600 °C for 1 hour, followed by placement in a desiccator with silica gel beads for 20 minutes, until reaching room temperature. The weight of the dried crucibles was determined, and 2 g of corn flour from each treatment was added to each one. The crucibles with the samples were maintained at 600 °C for 6 hours. After the allotted time, the crucibles were returned to the desiccator for 20 minutes and allowed to cool. The residue of ashes was weighed, and the data were recorded, with the weight of the empty crucibles subtracted to obtain the ash weight. To determine the percentage of ash in each sample, the following formula was applied:

$$\%Ash = \frac{Weightofresidue(g)}{Weightoffloursample(g)} * 100 \quad (7)$$

Quantification of soluble proteins

The colorimetric method by Bradford (1976) was employed to estimate the soluble protein content in the seeds. A calibration curve was constructed using bovine serum albumin (BSA, Sigma-Aldrich®) from a 0.5 mg·mL^{-1} stock solution. Aliquots of 25, 50, 75, and 100 µL were taken, diluted to a volume of 100 µL with distilled water, representing dilutions containing 12.5, 25, 37.5, and 50 µg of BSA, respectively.

Subsequently, 1 mL of Bradford reagent (Sigma-Aldrich®) was added to each dilution, and they were incubated at room temperature for 2 minutes. Absorbances were then determined using a UV-Vis spectrophotometer GENESYS™ 150 at 595 nm.

For protein extraction, 500 mg of whole grain flour was macerated in 5 mL of phosphate-buffered saline (PBS) extraction buffer in cold mortars. The mixture was centrifuged at 10,000 rpm for 10 minutes. The supernatant containing the extracted proteins was separated, and 100 µL aliquots were taken, to which 1 mL of Bradford reagent was added and incubated at room temperature for 2 minutes. Absorbances were read at 595 nm using a spectrophotometer. The results were compared with the BSA calibration curve, and the protein content was expressed as milligrams equivalent to albumin per gram of dry weight (mgEA·gdw^{-1}).

Oil content

The measurement of oil content relied on the 30-25 method (AACC 1995), involving extraction using a Soxhlet apparatus. Samples of 5 g of dehydrated whole grain flour were placed in cellulose thimbles and inserted into condenser tubes. Subsequently, 150 mL of petroleum ether (Golden Bell™) was added to the tubes, and the setups were placed on preheated magnetic stirrers with hotplate at ~70 °C. A cooling system, pumping water at 20 °C, was connected, and extraction took place for 6 hours. The recovered etheric extracts were stored at 4 °C until use. They were then double-filtered and concentrated by rotary evaporation at 60 °C/120 rpm until reaching a volume of ~5-10 mL, which was then deposited into pre-weighed glass vials. The extracts remained open at room temperature for 48 hours to evaporate the remaining solvent. The weight of the oil in milligrams (mg) per gram of dry weight (gdw) was determined using the following formula:

$$Oilcontent = \frac{Vialw/oil(mg) - Emptyvial(mg)}{Weightoffloursample(g)} \quad (8)$$

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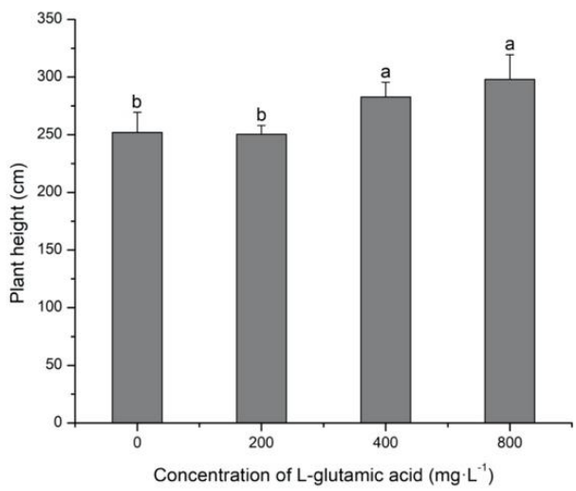
Statistical analysis

The statistical analysis was conducted using Analysis of Variance (ANOVA) and the Duncan Multiple Range Test (95.0%) to determine significant differences, employing Statgraphics Centurion XVI software. All tests were performed in triplicate.

Results and discussion

Height: The use of L-glutamic acid at concentrations of 400 and 800 $mg \cdot L^{-1}$ demonstrated a significant increase in the height of maize plants at 100 DAS, with an increment of 12.16% and 18.25%, respectively, compared to the control (Graphic 1).

The height of maize plants typically depends on the variety but can reach up to 4 meters (CONAHCYT, 2019). The increase in maize height usually does not exhibit significant effects when subjected to biostimulation (Blanco-Valdes *et al*., 2022), especially in hybrids, as size uniformity is a sought-after characteristic in plant breeding (Ibañez *et al.*, 2004). Nevertheless, the doses of L-glutamic acid used in this work proved to enhance the height of plants of the specific variety used. Maize plant height is also influenced by climatic and geological conditions during sowing (Gyenes-Hegyi *et al.*, 2002; Boomsma *et al.*, 2010; Liu *et al.*, 2021), water availability (Sari-Gorla *et al*., 1999), macronutrients (Iqbal *et al.*, 2015; Pedersen *et al.*, 2022), and the expression of certain genes (Pereira and Lee, 1995; Wu *et al.*, 2014).



Graphic 1 Height of maize plants (100 DAS). Mean ± SD. Different letters indicate statistically significant differences (Duncan, $P \leq 0.05$)

Weight

For the accumulation of plant biomass, the L-Glu 800 treatment had a significant effect increasing both fresh and dry weight values of the plants (Graphic 2).

The increase in plant weight has previously been linked to the exogenous application of amino acids. According to various studies, this can be associated with their effects on increased enzymatic activity, carbohydrate and nutrient content in leaves, and tolerance to adverse climatic conditions (Shehata *et al.*, 2011; Ragheb, 2016; Lee *et al.*, 2017; Noroozlo *et al*., 2019; Farahmandi *et al*., 2022). The shoot biomass of maize, whether fresh or dry, is utilized as forage in the livestock sector (Hanif and Akhtar, 2020), for cellulose production, ethanol, and biofuels (Manmai *et al*., 2021; Fu *et al*., 2022), or reintegrated into the soil for organic matter utilization in the no-till technique (Martínez-Gamiño and Jasso-Chaverría, 2005).

Ear size

The exogenous application of L-Glu did not significantly affect the size of maize ears in any of the three parameters evaluated in this study. Although the L-Glu800 treatment increased ear size by 12.34%, and L-Glu200 elevated values in diameter (10.2%) and the number of kernel rows (9.08%), no statistically significant differences were found in these variables (Graphic 3).

In comparison to results published in other studies involving exogenous amino acid applications (Rahgeb, 2016; Abdo *et al*., 2022), this study did not reveal a significant increase in ear dimensions. Similar results were obtained in the length and diameter of ears subjected to each treatment.

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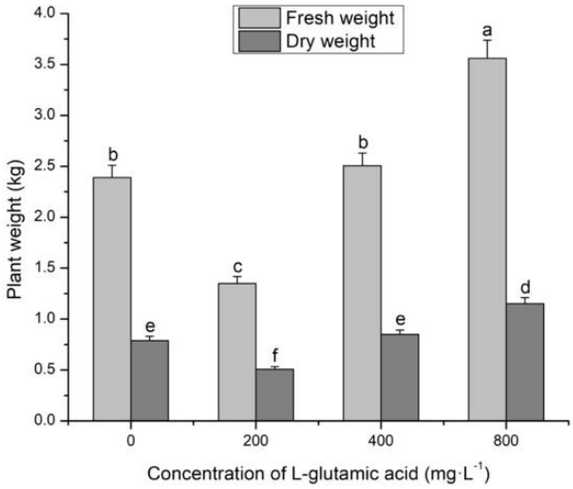
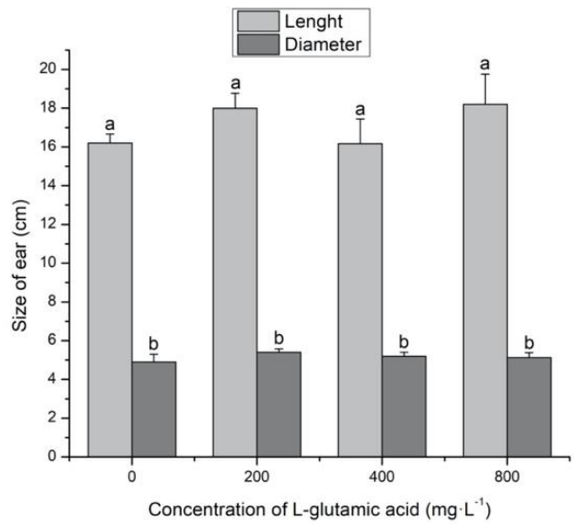


Graphic 2 Fresh and dry weight of maize plants (100 DAS). Mean ± SD. Different letters indicate statistically significant differences (Duncan, $P \leq 0.05$).



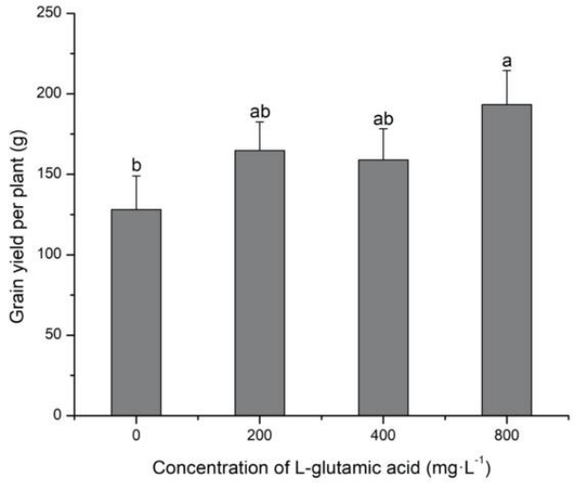
Graphic 3 Length and diameter of ears (140 DAS). Mean ± SD. Different letters indicate statistically significant differences (Duncan, $P \leq 0.05$)

Yield

Although there was no significant difference between the applied levels of L-Glu (Graph 4), an increase in yields was observed for ears from plants exposed to the amino acid compared to the control, especially with the L-Glu800 treatment, which rose by up to 49.98%.

One possible explanation for the crop yield increments is the relationship between L-Glu and factors such as increased photosynthetic rate and protein synthesis (Khan *et al*., 2012; Alfonsea-Simón *et al*., 2021; Báez-Pérez *et al*., 2022).

The results presented here are similar to those reported by Abdo *et al*. (2022), who achieved similar grain yields through biostimulation with humic acids and amino acids. The increase in agronomic crop yields due to amino acid application has been previously reported in various studies (Lee *et al*., 2017, Souri *et al*., 2017; Basanth and Mahesh, 2018).



Graph 4. Grain yield per plant (140 DAS). Mean ± SD. Different letters indicate statistically significant differences (Duncan, $P \leq 0.05$)

Weight of 100 seeds

The test for the weight of 100 seeds to determine grain size revealed that the application of 800 $mg \cdot L^{-1}$ of L-Glu acid produced the heaviest grains, and therefore the largest, with an average weight of 39.769 g, while the grains from the application of 400 $mg \cdot L^{-1}$ resulted in medium-sized grains, with an average weight of 33.512 g. On the other hand, the treatments of 200 $mg \cdot L^{-1}$ and the control produced small grains, with 27.482 g and 28.648 g, respectively, and there was no statistically significant difference between these two treatments (Graph 5).

In this study, an increase in the weight of 100 seeds was found as the L-glutamic acid dose increased, with a better response compared to other studies involving amino acid biostimulation in maize hybrids (Rahgeb, 2016; Abdo *et al*., 2022; Blanco-Valdes *et al*., 2022). According to Batistella *et al*. (2002), the weight of a thousand seeds based on the weight of a hundred seeds is the most convenient size classification method, even surpassing screening, regardless of the variety.

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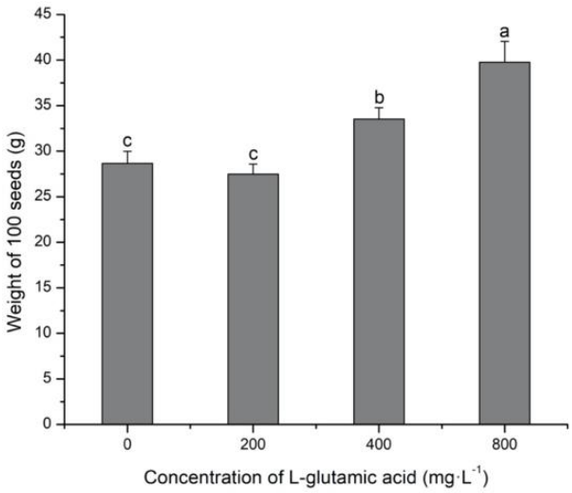
However, Peña-Betancourt *et al*. (2013) reported that, for example, some native maize varieties in Mexico can have an average weight of 100 seeds of 43.5 g, compared to the 29.8 g average weight in hybrid varieties.

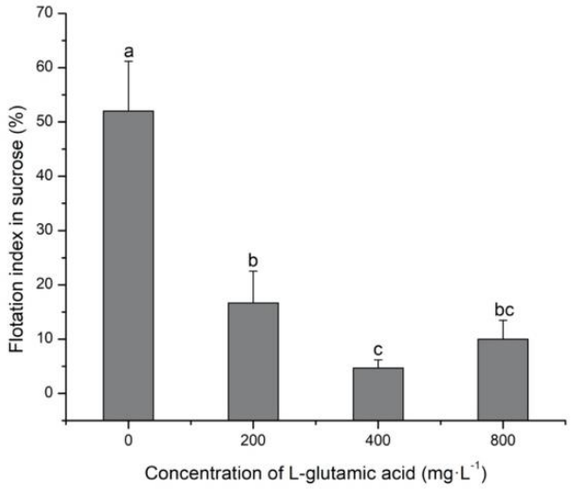


Graphic 5 Weight of 100 seeds (140 DAS). Mean ± SD. Different letters indicate statistically significant differences (Duncan, $P \leq 0.05$)

Flotation index

L-Glu applications significantly decreased the flotation percentage of seeds in a 67% sucrose solution. On average, seeds from plants treated with the increasing concentrations of L-Glu had flotation percentages of 16.6%, 4.6%, and 10%, respectively, well below the 52% of control seeds (Graph 6). From this, it can be suggested that exogenous L-Glu could be involved in increasing grain density, and consequently, its hardness.

In Mexico, flotation tests are a practical and indirect way to measure the hardness of maize grain, especially when it is destined for nixtamalization, as grains with high flotation indices denote lower yields for tortilla manufacturing. Generally, this parameter increases over time due to grain senescence or storage conditions (Odjo *et al*., 2022). When the flotation index is above 63%, it is considered a soft grain, between 38-62% is a medium-hard grain, and if it is below 37%, it is classified as a hard grain (Palacios-Rojas, 2018).



Graphic 6 Flotation index of seeds in 67% sucrose solution (ρ = 1.25 g·mL^{-1}). Mean ± SD. Different letters indicate statistically significant differences (Duncan, $P \leq 0.05$)

Germination rate and seedling size

Seed germination increased with two of the treatments. The application of L-Glu200 increased the germination rate by 30% compared to the control treatment, while the application of L-Glu400 increased it by 12.82%. On the other hand, L-Glu800 showed no significant difference (Graph 7). These results show a decrease in the germination rate as the administered dose of L-Glu increased.

Meanwhile, all three levels of L-Glu application significantly increased the size of the seedlings compared to the control (Graph 8). The highest averages were observed with the L-Glu400 treatment, where the complete seedlings reached an average length of 20.2 cm, the average cotyledon length was 6.34 cm, and the root length was 13.86 cm, values that were 4, 3.4, and 4.6 times higher than in the control (Figure 2).

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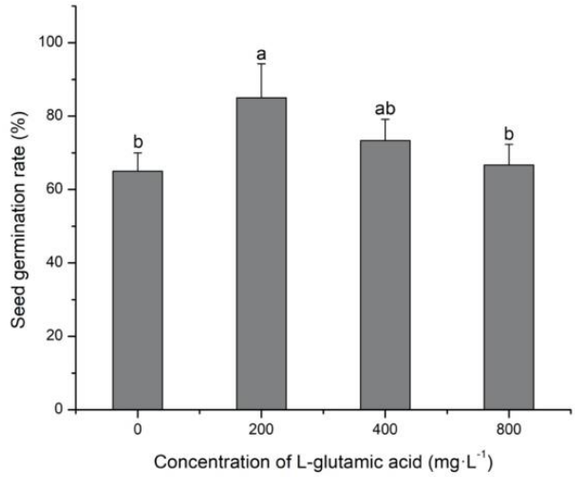
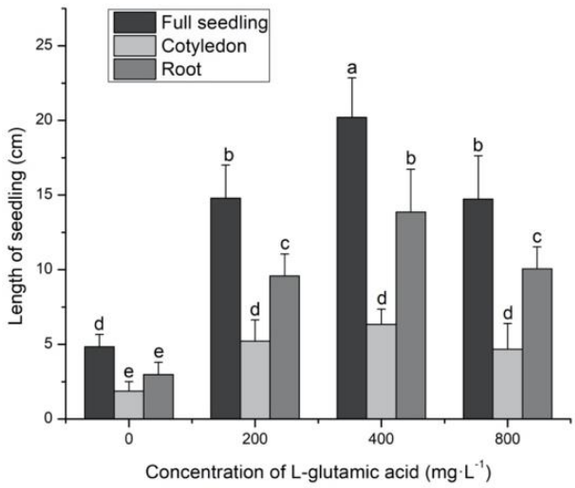


Graphic 7 Seed germination rate (7 DAS). Mean ± SD. Different letters indicate statistically significant differences (Duncan, $P \leq 0.05$)



Graphic 8 Length of seedlings (7 DAS). Mean ± SD. Different letters indicate statistically significant differences (Duncan, $P \leq 0.05$)

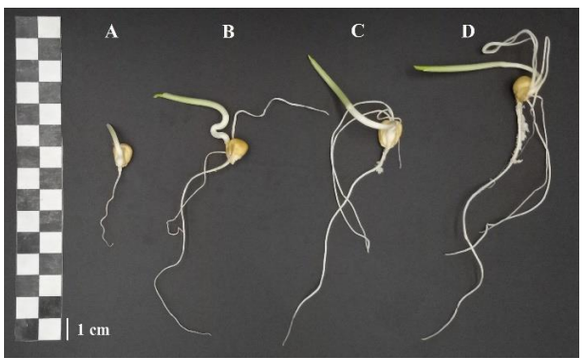


Figure 2 Comparison of maize seedlings with different treatments (7 DAS). A. L-Glu0; B. L-Glu200; C. L-Glu400; D. L-Glu800.

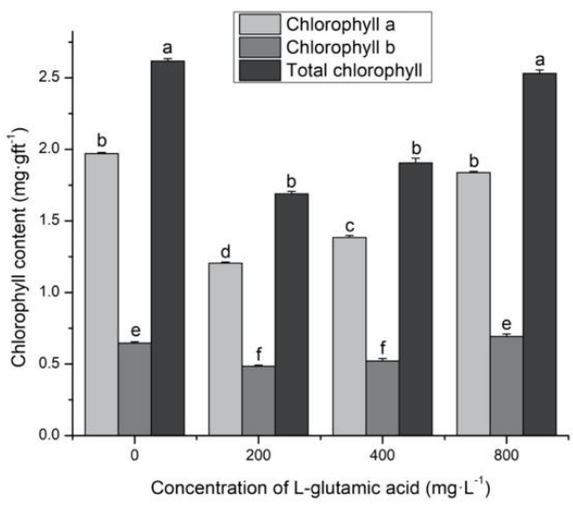
The direct effects of biostimulants on increasing seed vigor had been previously studied in other species, especially those biostimulants based on growth-promoting microorganisms (Colla *et al*., 2014; Cardarelli *et al*., 2022; Dong *et al*., 2020). Currently, there is limited information on the effects of amino acid biostimulation on seed germination (Makhaye *et al*., 2021), although some protein hydrolysates, such as collagen extract or bovine -hide gelatin, have been studied and found to promote germination and growth (Gaidau *et al*., 2013; Wilson *et al*., 2015; Niculescu *et al*., 2019).

Biochemical parameters

Chlorophylls

Evaluations of photosynthetic pigments (chlorophylls and carotenoids) revealed a decreasing trend in content in fresh leaves compared to the control, which showed the highest values for chlorophyll a (1.969 $mg \cdot g^{-1}$), total chlorophylls (2.616 $mg \cdot g^{-1}$), and total carotenoids (4.739 $mg \cdot g^{-1}$).

Chlorophyll an exhibited values below the control treatment in plants subjected to different concentrations of L-glutamic acid: 1.204 $mg \cdot g^{-1}$ with L-Glu200, 1.384 $mg \cdot g^{-1}$ in L-Glu400, 1.837 $mg \cdot g^{-1}$ in L-Glu800, representing a decrease of 38.85%, 29.71%, and 6.7%, respectively (Graphic 9). In the case of chlorophyll b, L-Glu800 showed the highest content (0.692 $mg \cdot g^{-1}$).



Graphic 9 Content of chlorophylls (100 DAS). Mean ± SD. Different letters indicate statistically significant differences (Duncan, $P \leq 0.05$)

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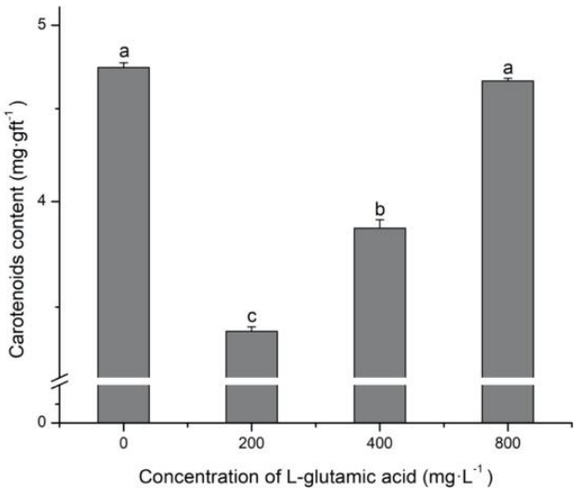
The total chlorophylls content (Graph 9) of the leaves revealed reductions in treatments with L-glutamic acid compared to the control (2.616 $mg \cdot g^{-1}$), with values of 1.689 $mg \cdot g^{-1}$ in the application of 200 $mg \cdot L^{-1}$, 1.906 $mg \cdot g^{-1}$ applying 400 $mg \cdot L^{-1}$, and 2.530 $mg \cdot g^{-1}$ in the treatment with 800 $mg \cdot L^{-1}$.

It is noteworthy that the content of chlorophyll a in plants is always higher than that of chlorophyll b, and a distinct trend can be observed in their values compared to other photosynthetic pigments. According to Serna-Rodríguez *et al*. (2011), the application of L-glutamic acid in plants increases the synthesis of chlorophyll b compared to chlorophyll a, resulting in greater photon capture, as chlorophyll b is part of the antennae responsible for light absorption.

Carotenoids

The quantification of total carotenoids (Graph 10) yielded information very similar to that obtained in the evaluation of total chlorophylls, where compared to the control, the L-Glu200, L-Glu400, and L-Glu800 treatments showed reductions of 28.4%, 18.4%, and 1.67%, respectively.

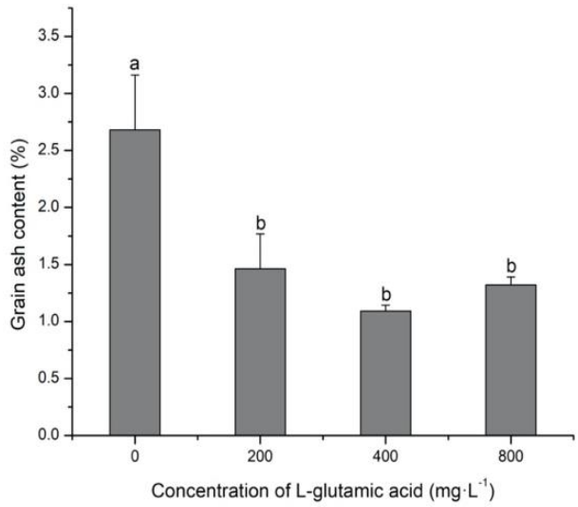


Graphic 10 Content of total carotenoids (100 DAS). Mean ± SD. Different letters indicate statistically significant differences (Duncan, $P \leq 0.05$)

Ash content

The results of this test showed a significant decrease in ash content in kernels across all three doses of L-Glu. For instance, the control had an ash content of 2.86%, which was 45.43% higher compared to the treatment with the closest content, in this case, L-Glu200, with 1.46%.

The other two doses yielded very similar percentages; for instance, L-Glu400 with 1.09%, and L-Glu800 with 1.32%, showing decreases of 59.3% and 50.7%, respectively (Graphic 11).



Graphic 11 Ash content in whole grain flour. Mean ± SD. Different letters indicate statistically significant differences (Duncan, $P \leq 0.05$)

Ash determination is very useful for assessing the total mineral content in a food item, which is not susceptible to evaporation, as is the case with water, or oxidation in the case of organic matter (Park, 1996). The ash content in plants can be primarily affected by the mineral characteristics of the soil or the use of agrochemicals (Rashid and Iqbal, 2012; Aslam *et al*., 2023). These ashes may contain substances such as heavy metals, silicates, sulfates, or phosphates. A low ash content would indicate a higher percentage of assimilable material as food and a lower amount of potentially toxic substances for living organisms (Marshall, 2010). Besides the food industry, this property is also desirable for biofuel production, as low inorganic matter content represents higher energy efficiency during combustion (Zając *et al*., 2020; Kukuruzović *et al*., 2023). In corn, ash content in seeds typically concentrates in the germ, and its values range between 1-3%, depending on the variety and other environmental conditions (FAO, 1985; Cázares-Sánchez *et al*., 2015; Bello-Pérez *et al*., 2016; Sinay and Harijati, 2021).

Protein content

L-Glu applications increased the amount of protein in the seeds of treated plants, especially with the 200 $mg \cdot L^{-1}$ dose, where an increment of 7.4% was observed.

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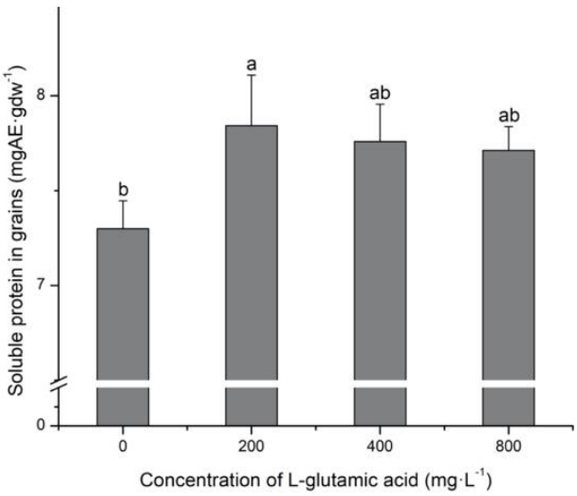
Likewise, the protein content showed a gradual decrease as the L-Glu doses of 400 and 800 mg·L^{-1} increased, with no significant difference compared to the control (Graphic 12).

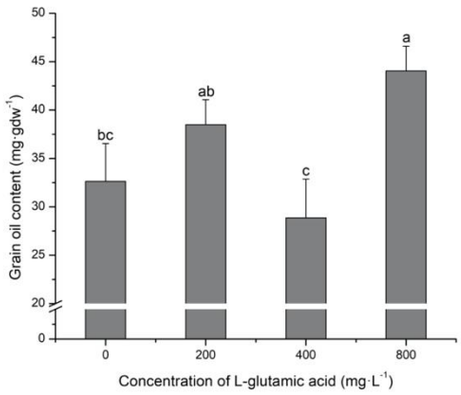


Graphic 12 Content of soluble protein in whole grain flour. Mean ± SD. Different letters indicate statistically significant differences (Duncan, P ≤ 0.05)

Given that it is a precursor for the synthesis of other amino acids and essential for polypeptide synthesis, the exogenous application of L-Glu can increase the protein content in plants. Previously, the effect of exogenous amino acid application on protein content in other plant species has been studied with positive results (Zhou *et al*., 2007; Haghighi *et al*., 2020). In crops such as Chinese hawthorn, lentil, tomato, and rice, L-Glu increased the soluble protein content when administered exogenously (Yu *et al*., 2010; Fardus *et al*., 2021; Lee *et al*., 2021; Luo *et al*., 2023). In maize, previous research had studied the effects of other biostimulants, such as valine, leucine, isoleucine, silicon, or salicylic acid, on protein content (Shaner and Reider, 1986; Moussa, 2006; Feng *et al*., 2022). Other factors influencing protein production in cereals may include planting density, soil conditions, fertilization, humidity, and temperature (Fowler *et al*., 1990; Casagrande *et al*., 2009; Chen *et al*., 2012; Széles *et al*., 2018).

Oil content

The lipid concentration in seeds increased when plants were subjected to applications of L-Glu200 and L-Glu800, although with significance only in the latter treatment, where the oil content was 35% higher than the control (Graph 13). On the other hand, L-Glu400 showed contents below the control treatment by up to 11.54%.



Graphic 13 Oil content in whole grain flour. Mean ± SD. Different letters indicate statistically significant differences (Duncan, P ≤ 0.05)

Hybrid corn seeds contain between 3-4% of oil, which is mainly concentrated in the germ and is rich in polyunsaturated fats and tocopherols (vitamin E), depending on whether it is white or sweet corn (Sanjeev *et al*., 2014; Ray *et al*., 2019). In Mexico, there are native varieties with a high oil content, where the percentage can rise to 5-6% (Torres-Morales *et al*., 2010; Guzmán-Maldonado *et al*., 2015). The lipid production in maize can be affected by variables such as temperature, planting location, humidity, or the expression of specific genes (Jellum and Marion, 1966; Shen *et al*., 2010; Veljković *et al*., 2018).

Conclusion

In general, it was observed that the application of L-Glu800, through seed treatment and foliar application in maize, increased the content of chlorophyll b, plant height, plant weight, grain yield per ear, and the weight of one hundred grains. On the other hand, no significant differences were observed in the effect of L-Glu on ear size. These studies on the biostimulating activity of L-glutamic acid allow us to refine existing alternatives that make it possible to increase the yield and quality of crops of agronomic interest. It is necessary to continue research efforts aimed at expanding the understanding of the application of free amino acids as plant biostimulants.

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Simulation of the leaf area index from thermal units of the cauliflower (*Brassica oleracea var*. Botrytis) crop

Simulación del índice de área foliar a partir de unidades térmica del cultivo de coliflor (*Brassica oleracea var.* Botrytis)

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Abstract

In the present research, the leaf area index (LAI) of the cauliflower crop was modeled, applying the thermal time concept, which was obtained from the threshold and optimal temperatures using a beta function, and then correlating it with the LAI using a growth function. The experimental design was a divided plot design where the large plots corresponded to 4 fertilization doses and the small plots to three planting densities and 4 repetitions. The leaf area index (LAI) was measured on a flat surface, using photographs of the leaves taken by a mobile device and analyzing them with the software (Image J) each photograph was scaled with a 5 cm reference line. For calibration, data corresponding to a high density (30,000 plants/ha) were used, finding the following adjustment statistics: bias (0.0047), RMSE (0.1152 m^2 m^{-2}), and EF (0.994). In the validation, data collected at a low density (26,000 plants/ha) were used and the following adjustment statistics were found: BIAS (-0.3541), RMSE (0.6774 m^2 m^{-2}) and EF (0.8358).

Thermal time, heat units, Growing degree days

Resumen

En la presente investigación se modeló el índice de área foliar (IAF) del cultivo de la coliflor, aplicando el concepto tiempo térmico, que se obtuvo a partir de las temperaturas umbrales y óptimas mediante una función beta, para después correlacionarla con el IAF mediante una función de crecimiento. El diseño experimental fue un diseño en parcelas divididas donde las parcelas grandes correspondieron a 4 dosis de fertilización y las parcelas pequeñas a tres densidades de plantación y 4 repeticiones. El índice de área foliar (LAI) se midió sobre una superficie plana, mediante fotografías de las hojas tomadas por un dispositivo móvil y analizándolos con el software (Image J) cada fotografía se escaló con una línea de referencia de 5 cm. Para la calibración se emplearon datos correspondientes a una densidad alta (30,000 plantas/ha), encontrándose los siguientes estadísticos de ajustes: sesgo (0.0047), RMSE (0.1152 m^2 m^{-2}), y EF (0.994). En la validación se emplearon datos recabados en una densidad baja (26,000 plantas/ha) y se encontraron los siguientes estadísticos de ajuste: BIAS (-0.3541), RMSE (0.6774 m^2 m^{-2}) y EF (0.8358).

Tiempo térmico, Unidades calor, Grados días de desarrollo

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Introduction

Cauliflower is a biennial plant belonging to the Cruciferae family, genus *Brassica*, species *Brassica oleracea* L., var botrytis, from which the predominantly white inflorescence, called pella, which forms at the base of the stem of the plant, is used (Fernández de Sousa & García González de Lena, 2016). Nationally, about 2,500 ha are established per year with an average yield of 19 t/ha. The main producing states in Mexico are: Hidalgo, Guanajuato and Aguascalientes (Zamora, 2016).

Temperature is one of the main driving forces for crop growth and development and several phenological stages are manifested through its development (Salazar Gutierrez, 2006; Salazar-Gutierrez & Chaves Cordoba, 2013). Cauliflower plants require more specific environmental conditions than other types of cabbage; their cultivation in an unsuitable environment requires climate modifications to meet the requirements of the different growth stages of the plant (Elahi et al., 2015).

Considering that leaves are responsible for intercepting radiation, a relationship has been found between relative light intensity and cumulative leaf area index, with light being exponentially extinguished as a function of increasing leaf area (Alberto et al., 2008). One of the most widely used methods is the accumulation of mean daily temperature above a base temperature (Tb), known as thermal time, growth or development degree days (DDD), heat units (Ángel López et al., 2010; Ruiz Corral et al., 2002). or physiological time, and is defined as the number of degree days required to complete a given developmental process or phenological stage (Trudgill et al., 2005). Agroclimatic models have been developed that relate the different phenological phases to the thermal time or physiological time of the plant (Parra Coronado et al., 2015). The objective of the present work was to calibrate and validate a mathematical model that allows estimating the IAF dynamics based on thermal time for two cauliflower crop densities.

Materials and Methods

Location of the experiment

The experimental site was located in Xochimilco, municipality of Tecamachalco in the state of Puebla, with coordinates 18º 50' 34.7" North latitude and 97º 44' 40.4" West longitude. A cauliflower (Brassica Oleracea L.) open field crop was established on the land of a cooperating farmer in the aforementioned locality. With the help of agricultural machinery and implements, the fallow was carried out, and the land was furrowed twice, followed by the formation of the cultivation beds, which were 0.9 m apart and approximately 100 m long. The characteristics of the irrigation tape used were as follows: 16 mm ID, 6 mil gauge, 10 cm spacing, 1 lph @ 0.55 BAR, 3,050 m length, Rivulis® brand. The tape was placed only in a single row and fastened with wooden stakes at the end of each planting bed.

Experimental design

The experimental plot consisted of a length of one hundred metres long by twenty-five metres wide, the experiment dealt with four treatments, with different doses of fertilisation (F1, F2, F3, F4). The experimental unit was then divided into four parts, each of these parts was called a "replicate", so there were four replicates (R1, R2, R3, R4). Each repetition in the same way will be divided into twelve parts, which were called "densities" these had a length of 8 meters long by 5. 4 metres wide, three densities were considered: D1= 25,000 plants/ha (43 cm separation between plants), D2= 28,000 plants/ha (40 cm), D3= 30,000 plants/ha (37 cm), in a horizontal way the densities were represented, and in a vertical way the treatments (F1,F2,F3,F4), obtaining the following combinations: (F1xD1, F1xD2, F1xD3), (F2xD1, F2xD2, F2xD3), (F3xD1,F3xD2, F3xD3) and (F4xD1,F4xD2, F4xD3), with 4 replications, each experimental unit had a width of 5. 4 m wide and 8 m long (area of 43.2 m^2). Of these combinations, only the combinations (F3xD1 and F3D3), consisting of a medium-high fertilisation rate and low and high densities, were considered for modelling the leaf area index. Fertilisation was applied in three split applications: bottom application (33.3%), one month after transplanting (33.3%) and one and a half months after transplanting (33.3%).

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Crop variables

The leaf area index (LAI) was measured in the laboratory using a flat surface on which a five centimetre reference line was marked and then used to support the scaling of the images, which was applied to each photograph of the leaves using the software (Image J). Each plant had to be carefully detached. These leaves were placed on a flat surface, in a strategic manner, in such a way as to cover the exposed area of each leaf for each photograph taken, as well as with their respective identification label. For this purpose, a vertical base (tripod) was installed to support the camera for the capture of the images.

Temperature measurement

During the cultivation cycle, a HOBO climatic station (HOBO Onset Bourne, Massachusetts, USA) was installed in which the air temperature was recorded, using a sensor model STM-B-M008 (HOBO, Onset), which was measured every minute and averaged on an hourly basis.

Simulation of leaf area index (LAI)

To simulate this variable, a modification was made to the functions originally used by the HORTSYST model (Martinez-Ruiz 2019 and 2021), so that it could be extended to open field crops, as in the case of the crop under analysis. This variable was obtained by multiplying the (ºC d), obtained with a Gompertz equation, by the planting density (d). For this, the thermal time (, °C) was calculated, applying the beta function (Zhou & Wang, 2018), defined as the relationship between the growth rate and the conditions of the actual, optimum and base temperature. As described below.

$$LAI_{j+1} = LA_j * d \quad (1)$$

$$LA_j = p5 * \exp\left(-\exp\left(p6 - \left(p7 * TT_{j+1}\right)\right)\right) \quad (2)$$

$$TT_{i+1} = \begin{cases} 0; & T_{a,i+1} < T_b \\ \frac{(T_{a,i+1}-T_b)}{(T_o-T_b)} \frac{(T_u-T_{a,i+1})}{(T_u-T_o)}^{\frac{(T_u-T_o)}{(T_u-T_b)}} (T_o - T_b); & T_b \leq T_{a,i+1} \leq T_u \\ 0; & T_u < T_{a,i+1} \end{cases} \quad (3)$$

$$TT_{j+1} = \left[\sum_{i=1}^{24} TT_{i+1}\right]/24 \quad (4)$$

Where, LA_j is the leaf area on the -th day, TT_{i+1}y TT_{j+1} represents thermal time in the hour $i+1$ y of day $j+1$ next, LAI_{j+1} is the leaf area index of the following day, is the planting density, $T_{a,i+1}$, T_b, T_o, T_u is the air temperature in the next hour, base temperature (T_b=10 ºC), lower optimum temperature and upper optimum temperature, respectively. The parameters $p5$, $p6$ y $p7$ se were estimated during calibration, applying the non-linear least squares method.

This model to predict leaf area index was calibrated at a high density of 30,000 plants/ha and validated for a density of 26,000 plants/ha.

Results and Discussion

Figure 1 shows the average daily air temperature during the cauliflower growing cycle, with a minimum temperature of 12 °C 5 days after transplanting, corresponding to February, a maximum temperature of 25 °C for May and an average temperature of 18 °C. The temperature drop of 12 °C during the growing cycle of cauliflower was observed for the month of May. The temperature drop of 12 °C that was recorded is due to the fact that the month of February belongs to the winter season, therefore, the days are susceptible to sudden changes in temperature, in fact, winter ends 40 days after transplanting and after those days the temperature increase was observed with the onset of spring.

Figure 2 shows the calibration of the simulated LAI with respect to the measured LAI, it can be seen that the simulated curve has an accurate trend with respect to the measured values. On the other hand, Figure 2B shows the 45° line (1:1 line) where the simulated data points are on this line due to the accuracy of the calibration process.

For the validation of the model it can be seen in Figure 2C that the simulated LAI curve with respect to the measured LAI points there is a bias approximately at 70 DAT and 85 DAT, this anomaly can be clearly identified by the 45° line. In Figure 2D the simulated LAI given by the model tends to overestimate with respect to the measured ones. The observed systematic error of the measured LAI may be a cause of a sampling error at the time of plant selection.

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For the model studied, the following model fit statistics were found: In the calibration, a value for BIAS of 0.0047, RMSE (0.1152) and EF (0.994) were found, and in the validation of: BIAS (-0.3541), RMSE (0.6774) and EF (0.8358). in the calibration the result close to zero for the BIAS indicator shows that there is no considerable bias and the predicted values are accurate, contrary to the validation in which a negative result was obtained, which indicates that the LAI is being overestimated by the model. For the RMSE indicator in the calibration it resulted in a small value, not so for the validation, however, the value of this statistic is statistically acceptable as it is above 80%. On the other hand, the EF indicator in both calibration and validation both resulted in acceptable values, which indicates that the estimation of the parameters was performed with excellent computational efficiency. This fact is in agreement with what Zhou & Wang, (2018) mentioned that accurate estimates of degree development days (DDD) are important in models that simulate crop growth and for field crop management. Where they found that the use of DDD greatly improved the description and prediction of phenological events compared to other approaches, such as time of year or number of days, especially for describing crop phenology and developmental stage, they found that the use of DDD greatly improved the description and prediction of phenological events compared to other approaches, such as time of year or number of days, especially for describing crop phenology and developmental stage.

On the other hand, Ángel López et al. (2010) mention that phenological models are tools designed to know and predict plant development and they used the Euler method for the simulation of nodes and phenological development of the plant through thermal time. They found a value of RSME = 0.28. Trudgill et al. (2005) proposed a phenological model for feijoa cv. Quimba, in which the base temperature (Tb) is estimated for four different reproductive phenological periods and its duration in terms of DDD, to predict the dates of anthesis, fruit set and harvest. Besides relating leaf area to thermal time, other authors such as Kresnatita et al. (2020) found that leaf area is strongly related to dry weight of cauliflower plants (R2 = 96 and 97 %). The parameter values found during the calibration process were: p5 = 3, p6 = 2.2112 and p7 = 0.0025.

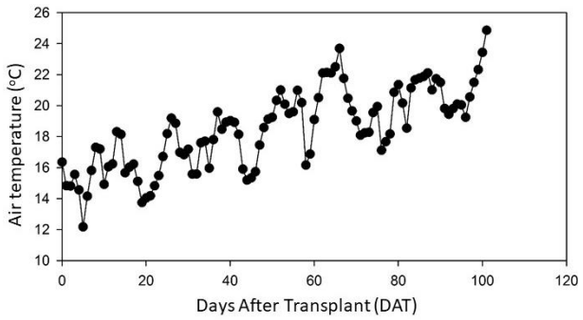

Figure 1 Average air temperature of the experimental site Xochimilco, Puebla

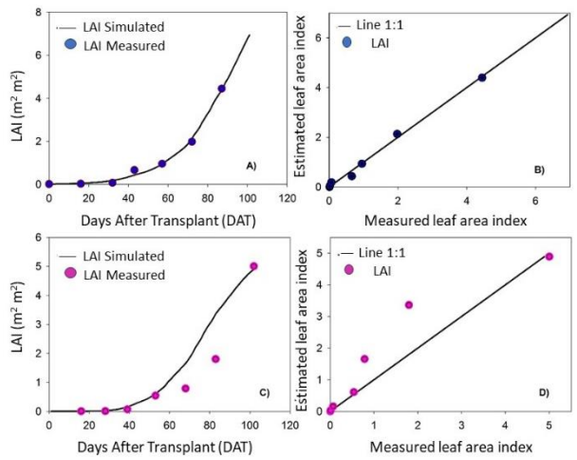

Figure 2 Simulation of leaf area index of cauliflower crop A) calibration, C) validation, B and D) line 1:1

Conclusion

The calibration and validation of the mathematical model presents a good fit for the study conditions, although its evaluation in other locations with different environmental conditions is recommended. Finally, it is important to make sure in each sampling that the selected plants are representative of the whole field, otherwise, the model fit may not be as expected for its application for more general conditions. The thermal time to track phenological stage changes is a fairly accurate and acceptably robust concept.

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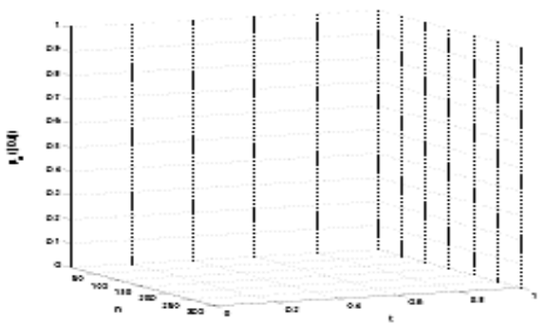

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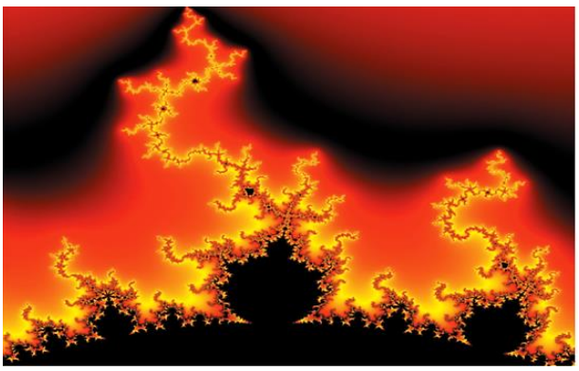

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