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Effect of Adding Mineral Fertilizer NPK and Biochar on the Potential Buffering Capacity of Potassium and its Relation to Corn Yield in Calcareous Soil in Northern Iraq

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Abstract. To study the state of potassium in the soil using the intensity and capacitance relationships, and to find out the effect of adding mineral fertilizers NPK and biochar on the dry weight of the vegetative part and seeds, as well as on the potassium content in the vegetative part and seeds of corn crops, we chose the field of the College of Agriculture and Forestry at the University of Mosul. The field was divided into nine blocks with three replications according to a randomized complete block design. Urea was used as a source of nitrogen at three levels (0, 160, 320) kg h^{-1}, while potassium sulfate was added as a source of potassium at three levels (0, 40, 80) kg K_2O h^{-1}, and also tri-superphosphate fertilizer was used as a source of phosphorus at three levels (0, 100, 200) kg ha^{-1}, noting that nitrogen was added in two batches, the first before planting and the second batch a month after germination. Biochar was added at three levels: %0, %1, and %2. The results indicated that the values of the ionic activity ratio ranged between (0.056 -0.141) mol. $L^{-0.5}$, while the values of labile potassium ranged between (2.980-7.852) Cmolc.kg-1, and the free energy values ranged between (-1705.371**)** cal. mole $kelvin^{-1}$ and **(**-1160.957) cal. mole $kelvin^{-1}$, whereas the values of the Potential Buffering Capacity ranged between (45.346 -55.737) $Cmolc.kg^{-1}/mol^{-1}.L^{0.5}$. The results also showed that the addition of mineral fertilizer and activated charcoal led to an increase in the dry weight of the vegetative part from (15816.29) kg h^{-1} in the comparison treatment (F_0B_0) to (31848.67) kg h^{-1} in the treatment (F_2B_2) and an increase in the dry weight of the seed from (3455.83) kg h^{-1} in the comparison treatment (F_0B_0) to (8092.50) kg h^{-1} in the treatment (F_2B_2). Also, the addition of mineral fertilizer and activated charcoal increased the potassium content in the plant from (171.35) kg h^{-1} in the control treatment (F_0B_0) to (551.13) kg h^{-1} in the treatment (F_2B_2) and increased the potassium content in the seeds from (37.45) kg h^{-1} in the control treatment (F_0B_0) to (140.03) kg h^{-1} in the treatment (F_2B_2).

Keywords. Maize Crop, Q/I, Potassium, Calcareous soil.

1. Introduction

Potassium is one of the main nutrients of the plant [1], as it activates more than 80 enzymes inside the plant, in addition to its role in opening stomata, regulating the osmotic potential, and increasing the permeability of plant cells, as well as increase plant growth and production [2]. The high content of calcium carbonate in Iraqi soils may lead to hindering the absorption of potassium due to the presence of calcium ions in high quantities in the soil solution. Iraqi soils are also characterized by their high content of clay minerals 2:1, which work on the stabilization of high quantities of available potassium and convert it into a slow available form [3].The use of traditional standards in evaluating the availability of potassium did not achieve the purpose of its use in many cases [4], so the researchers tended to use thermodynamic standards that are considered A sound input in assessing the availability of potassium in the soil [5]. [6] indicated the success of evaluating potassium availability in many Iraqi soils using thermodynamic criteria that included ionic activity, potassium activity coefficient, intensity-capacity relations (Q/I), free energy, and potassium regulatory capacity. [7,8] and [9] see that the state of dynamic equilibrium of potassium between the solid and liquid soil phases depends on the concept of ion exchange according to the law of ratios for potassium, calcium, and magnesium ions and that this ion exchange is one of the important physiochemical methods. To identify the availability of potassium by obtaining some thermodynamic parameters that help to understand the state of soil fertility in order to determine the fertilizer requirements for potassium [10,11].

2. Materials and Methods

The field of the College of Agriculture and Forestry / University of Mosul / Iraq was chosen to carry out an agricultural experiment, where composite samples were taken from the field soil and their chemical and physical properties were estimated as shown in Table (1). The field was divided into 9 boards, with an area of one square meter for each board, and with three repetitions, according to the randomized complete block design. After that, the yellow corn seeds were planted in holes, with 25 holes in each plate, and the distance between one hole to another was 25 cm. Then the mineral fertilizer NPK and biochar were added to the soil, where urea was added as a source of nitrogen at three levels (0, 160 and 320) kg h-1, while potassium sulfate was added as a source of potassium at three levels as well (0, 40 and 80) kg h-1, and triple superphosphate fertilizer was also added as a source of phosphorus at three levels (0,100 and 200) kg h-1, noting that nitrogen was added in two batches, the first before planting and the second batch a month after germination. The panels have been treated with the following treatments:

Control	F0B0
Zero NPK + 1% biochar	F0B1
Zero NPK + 2% biochar	F0B2
50% of the recommended NPK + Zero biochar	F1B0
50% of the recommended NPK + 1% biochar	F1B1
50% of the recommended NPK + 2% biochar	F1B2
100% of recommended NPK + Zero biochar	F2B0
100% 0f recommended NPK + 1% biochar	F2B1
100% 0f recommended NPK + 2% biochar	F2B2

Finally, plant samples were taken at the harvest stage to calculate the dry weight of the vegetative part and seeds and estimate the potassium content of the vegetative part and seeds.

Table 1. Some chemical and physical properties of the study soil.

Properties	Unit	Value
pH	---	7.8
EC	dSm^{-1}	0.9
$CaCO_3$	$g\ kg^{-1}$	250
O.M.	$g\ kg^{-1}$	17.5
dissolved potassium	Centimol kg $soil^{-1}$	0.4
CEC	Centimol kg $soil^{-1}$	17.5
available potassium	$mg\ kg^{-1}$	330
Sand	$g\ kg^{-1}$	460
Clay	$g\ kg^{-1}$	215
Silt	$g\ kg^{-1}$	325
Texture	Loam	

Thermodynamic parameters were estimated before and after planting using intensity and capacity relationships according to the concept of [10] by adding a potassium chloride solution at

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concentrations of (0, 0.1, 0.2, 0.4, 0.6, 0.8, and 1) mmol.ionL-1 in a ratio of 1 soil: 20 solution with Shake for an hour and leave for 24 hours at a temperature of 298±1°C. Dissolved potassium was measured using a flame photometer and an electrical conductivity device, and calcium and magnesium were measured by titration with EDTA.
Adsorbed potassium: Adsorbed potassium was calculated on the solid soil phase according to the following equation:

Adsorbed potassium = concentration of ion added - (concentration of ion in the equilibrium solution) * volume of solution / mass of soil (1)

The ionic activity coefficient was calculated by the modified Davies equation given in [12] and states:

$$-logfi = \frac{Azi^2\sqrt{I}}{1+\sqrt{I}} - 0.3I \quad (2)$$

Where:
A = constant magnitude = 0.0509
Zi^2 = square charge of the ion
I = the ion strength of the equilibrium solutions ($mol.L^{-1}$), which was calculated by the equation [13]:

$$I = 0.013EC \quad (3)$$

The ionic activity values were calculated according to the following equation:

$$ai = ci*fi \quad (4)$$

where:
ai = ionic activity, which was calculated according to the Lewis equation as reported by [14]
ci = potassium concentration measured in $mol.L^{-1}$units
fi = ionic activity coefficient
The intensity of ions in the liquid soil phase: It was calculated according to the concept of the law of proportions proposed by him [10] and according to the following equation:

$$AR_k = \frac{aK}{\sqrt{a(Ca+Mg)}} \quad (5)$$

Where its value was plotted on the x-axis, while ±Δk was plotted, which was calculated from the difference in potassium concentration before and after equilibrium on the y-axis of the intensity and quantity curves, through which it can be calculated:

- Labile potassium Δk : from the extension of the region facing the y-axis.
- Potassium activity ratios at ARK equilibrium: represents the I/Q meeting point with the x axis.
- Calculating the exchanged free energy -ΔG according to the following equation [15].

$$-\Delta G = 2.303\ RT \log ARK \quad (6)$$

- Calculating the potassium regulatory capacity of PBCk by dividing Δk by ARK.

3. Results and Discussion

The slope and behavior of the Q/I relationship shown in Figures (1, 2) is a distinctive characteristic of each soil and describes the behavior of the nutrient element and the dynamics of potassium adsorption and release, which reflects the difference in the regulatory capacity of the soil for food processing, and is evident from the difference in soil parameters in the values of its slope coefficient and secant values, and this it is related to the difference in the added fertilizer treatments and the different ion forms, and the upper part of the curve, which is linear, allows for the estimation of the ionic effectiveness ratio at equilibrium (ARione), and through it, it is possible to know the location of adsorption, whether it is superficial or within the layers, as well as the ability of the soil to regulate against potassium depletion, which was derived from these curves. It is also clear from Figures (1,2) that the straight part in it expresses the exchanged ion that is liberated from easy-to-ready sites, while the curved part clearly indicates the ion liberated from sites that are held more tightly, and these sites are called specialized sites[16]. All equations shown in Figures (1, 2) clearly indicate the strength of the

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correlation between the intensity of the added nutrient in the balance solution with its quantity in the solid soil phase and for all added fertilizer treatments.

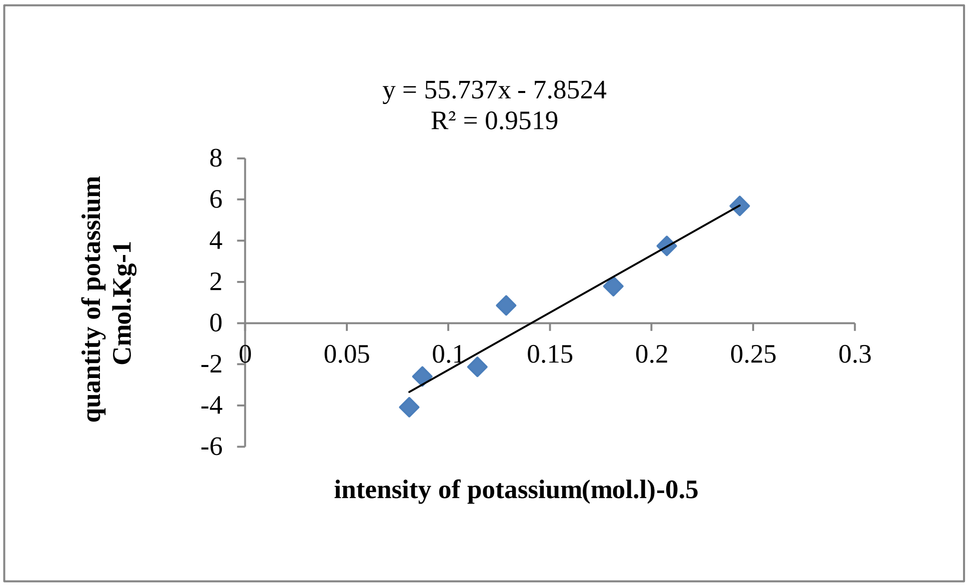

Figure 1. The intensity and quantity , Relationships of potassium in the study soil before planting.

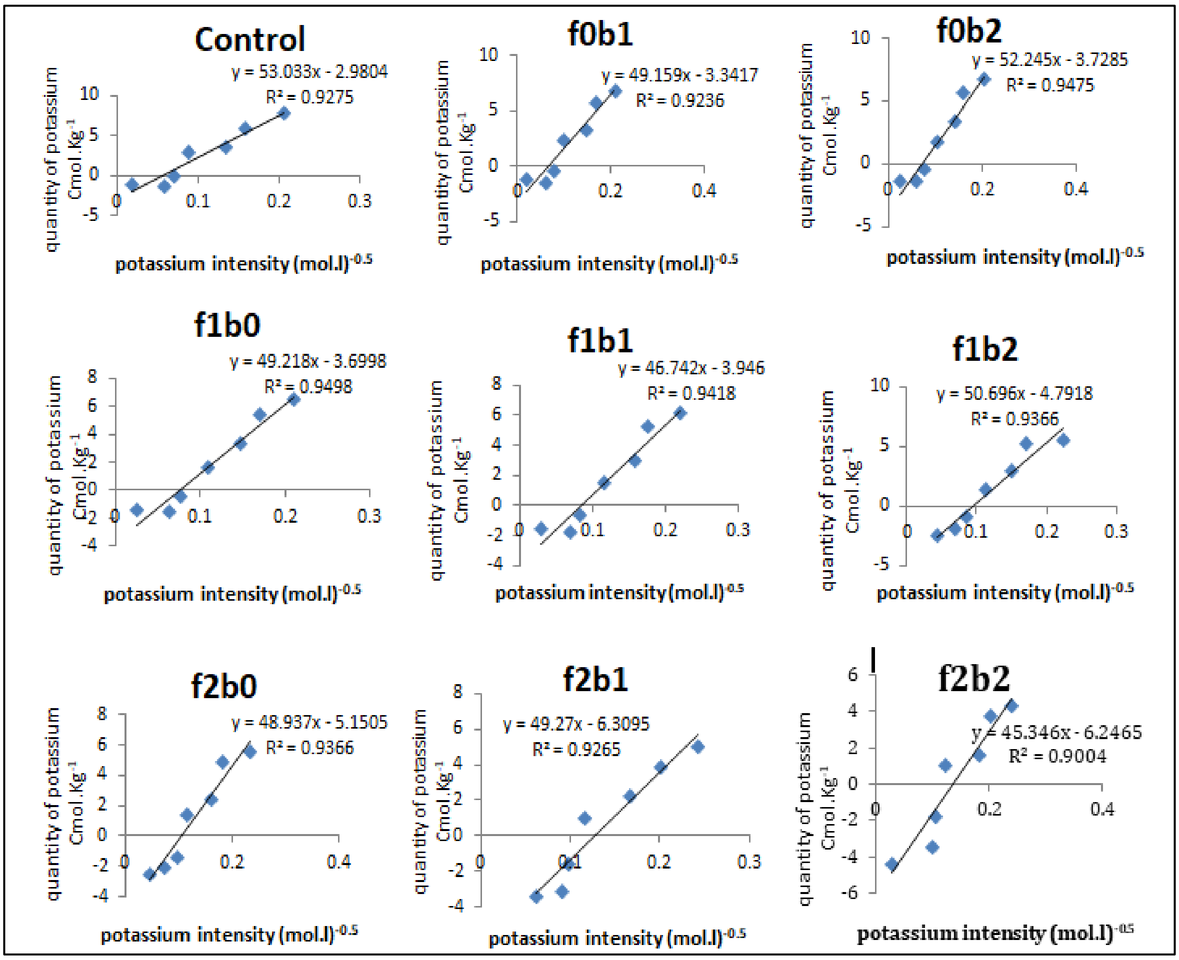

Figure 2. The intensity and quantity Relationships of potassium in fertilizer treatments after planting.

3.1. Ionic Activity Ratios

The values of the ionic activity ratios were used to detect adsorption sites, as the results shown in Table (2) indicate that the values of the ionic activity ratios, which express the intensity of the ion in the liquid soil phase when no gain or loss from the soil occurs, amounted to (0.141) mol $L^{-0.5}$ before planting, while after planting it ranged from (0.056) mol $L^{-0.5}$ in the comparison treatment (f_0b_0) to (0.138) mol $L^{-0.5}$ in the treatment (f_2b_2), at a rate of (0.096) mol $L^{-0.5}$. These values indicate that adsorption into the study soil occurred at planar positions according to the theory of [17], which indicated that values of effectiveness rates were less than (0.01) mol $L^{-0.5}$, indicates the dominance of adsorption on the edge sites, while values greater than 0.01 mol $L^{-0.5}$ refers to the dominance of adsorption on the surface (Plannar Positions) and that the process of fertilizing these soils with the nutrient element will be exposed to an adsorption process on these sites, making it moderate to slow availability during the agricultural season. These values are a measure of the instantaneous soil content and also indicate the ion intensity in the liquid phase of the soil, which has the ability to supply the ion over a long period of time.

Table 2. values of free energy ratios, ionic activity and potential buffering. The capacity of potassium for fertilizer treatments in the study of soil.

Fertilizer transactions	**Potential buffering capacity $Cmol_c.Kg^{-1}/mol^{-1}.L^{0.5}$**	**Labile potassium $Cmolc.Kg^{-1}$**	**Ionic activity ratios $mol.L^{-0.5}$**	**Free energy cal mol $kelvin^{-1}$**
f2b2	45.346	6.247	0.138	-1174.271
f2b1	49.270	6.310	0.128	-1217.490
f2b0	48.937	5.151	0.105	-1333.703
F1b2	50.696	4.792	0.095	-1397.384
f1b1	46.742	3.946	0.084	-1464.322
f1b0	49.218	3.699	0.075	-1533.190
f0b2	52.245	3.729	0.071	-1563.840
f0b1	49.159	3.342	0.068	-1592.655
f0b0	53.033	2.980	0.056	-1705.371
before planting	55.737	7.852	0.141	-1160.957
average	50.038	4.805	0.096	-1414.318

3.2. Labile Potassium

This value represents the number of ions present on the adsorption surface, which type is (Planar Surface Panda) [18] [19]. The mobile potassium values before planting were (7.852) $Cmolc.kg^{-1}$, while after planting they ranged from $Cmolc.kg^{-1}$ (2.980) in the treatment (F_0B_0) to (6.247) $Cmolc.kg^{-1}$ in the treatment (F_2B_2), with an overall average of (4.805) $Cmolc.kg^{-1}$. The mobile ion values provide a measure of the percentage of the ion associated with non-specialized sites, and high values mean high release into the liquid phase of the soil, and soils that contain a limited number of adsorption sites are characterized by high activity; Therefore, clay minerals in soil contribute to increasing the number of specialized and non-specialized sites responsible for ion adsorption and their retention on the adsorption surface [17]. That is, soft soils that have a high adsorption capacity need more ions to provide the plant with the amount required for its growth, while coarse-textured soils needs a lower amount of ions to reach the highest dissolved concentration in the soil solution, despite not having sufficient reserves to provide the plant with the required amount during the crop growth period [20] [21].

3.3. Free Energy

The results shown in Table (2) indicate that the free energy values for the state of thermodynamic equilibrium at a temperature of 298 Kelvin were negative values, which indicates the spontaneity of the reaction, as its value before cultivation was (-1160.957) calorie mole $kelvin^{-1}$, while after cultivation it ranged from (-1705.371) calorie mole $kelvin^{-1}$ in treatment (f_0b_0) to (-1174.271) calorie mole $kelvin^{-1}$ in treatment (f_2b_2) and as an average (-1414.318) calorie mole $kelvin^{-1}$. The change in free energy values between soils is directly related to changes in the equilibrium conditions of the soil solution with its solid phase. According to the classification proposed by the scientist [15] in determining free energy, the study soil suffers from a deficiency in potassium preparation and that the preparation process is an automatic process because all free energy values are negative.

3.4. Potential Buffering Capacity

This value is a criterion for the ability of the soil to maintain the ion potential against any process of depletion from the liquid and solid phases of the soil. Although the speed of release of this element from the non-exchanged phase to the exchangeable phase cannot be measured from capacity and intensity relationships, it is possible to measure the soil's ability to maintain On the change that occurs to the ions, which makes it give an indicator of liberation [22] [23]. The value of the potassium potential regulatory capacity before planting was (55.737) $Cmole.kg^{-1}/mol^{-1}.\ L^{0.5}$, while after planting it ranged from (45.346) $Cmole.kg^{-1}/mol^{-1}.\ L^{0.5}$ in the (F_2B_2) treatment to (53.033) $Cmole.kg^{-1}/mol^{-1}.\ L^{0.5}$ in treatment (F_0B_0) at a temperature of 298 degrees kelvin, with a general average of (50.038) $Cmole.kg^{-1}/mol^{-1}.\ L^{0.5}$. High values of the regulatory capacity of the ion potential express a stable availability for it over a long period, in contrast to low values. The differences in the values of the regulatory capacity between fertilization treatments may be attributed to the role of low-molecular-weight organic molecules in the release of potassium from biochar [24].

3.5. Effect of Adding NPK Chemical Fertilizer

The results in Table (3) indicate that adding NPK mineral fertilizer led to an increase in the dry matter production of the yellow maize crop from 15816.29 kg ha^{-1} in the comparison treatment to 31848.67 kg ha^{-1} in the f_2b_2 treatment, as well as the dry matter of the yellow maize seeds from (3455.83 to 8092.50) kg ha^{-1}. The addition of mineral fertilizers and activated charcoal increased the potassium content in the vegetative part from 171.35 kg ha^{-1} in the comparison treatment to 551.13 kg ha^{-1} in the f_2b_2 treatment, and the potassium content in the seeds from 37.45 kg ha^{-1} to 140.03 kg ha^{-1} respectively, which clearly indicates the importance of mineral fertilizers and activated charcoal in dry matter, seed production and potassium content in each of them. The reason may be the presence of mineral fertilizers with biochar, which reduces the C/N ratio and thus increases the efficiency of mineral fertilizers for the plant on the one hand. On the other hand, the presence of biochar with NPK will lead to an increase in the efficiency of its consumption by the plant and thus is reflected in raising its dry matter productivity. This is consistent with the results of [25], who pointed out the importance of activated charcoal in raising corn crop productivity.

Table 3. Effect of mineral fertilizer and activated charcoal on potassium uptake by plants and maize seeds.

Fertilizer transactions	Dry matter kg h^{-1}		Potassium content kg h^{-1}	
	Vegetative part	Seeds	vegetative part	Seeds
f_2b_2	31848.67	8092.50	551.13	140.03
f_2b_1	29192.83	7236.67	460.35	114.11
f_2b_0	26963.67	6521.67	406.23	98.26
F_1b_2	25393.04	6153.33	376.66	91.28
f_1b_1	24688.00	5904.17	359.62	86.00
f_1b_0	23657.67	5470.83	325.71	75.30
f_0b_2	21122.17	5005.00	279.54	66.24
f_0b_1	18187.33	3965.00	215.26	46.92
f_0b_0	15816.29	3455.83	171.35	37.45

The results in Figures (3, 4, 5 and 6) indicate a significant correlation between the thermodynamic indicators of the potassium ion and its role in the production of vegetative dry matter and seed yield for the yellow corn crop. The highest coefficient of determination appeared at the free energy values, followed by the potassium ion effectiveness ratio at equilibrium and potassium mobile and regulatory capacity at equilibrium, respectively, which gives a clear indication that the yellow corn crop benefits from dissolved potassium first due to its easy movement to the plant roots, and then the plant roots tend to deplete the potassium adsorbed on the soil surface, which is expressed as mobile potassium. The low values of the coefficient of determination for the processing capacity of potassium compared to the free energy and the potassium effectiveness ratio and mobile potassium clearly reveal to us the role of the dissolved and exchangeable form of the potassium ion in immediate food processing or the short periods of the growth stage of yellow corn, while the role of the regulatory capacity is slow for food processing in the short term and this is due to the processes of fixing potassium between the layers within the hexagonal gaps, and thus the difficulty of its release towards the plant roots, due to the presence of an abundance of nutritional ions in the soil, which therefore makes the plant tend to biologically absorb sites that are easy to absorb (soluble and mutual). This is consistent with what was found by [26] in an experiment Fertilizing yellow corn with potassium sulfate fertilizer for different soils from Sulaymaniyah Governorate, northern Iraq, and supports the findings of [18], in their study on evaluating some Iraqi soils using intensity and capacity criteria.

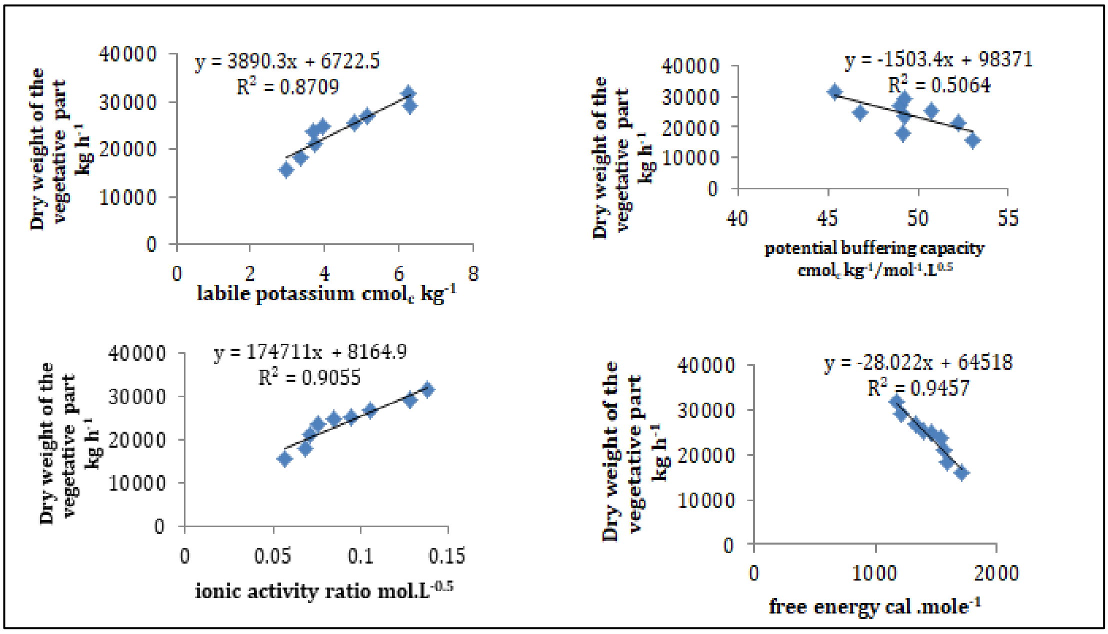

Figure 3. The relationship between thermodynamic parameters of potassium ion and dry matter yield in the vegetative part of yellow corn plant.

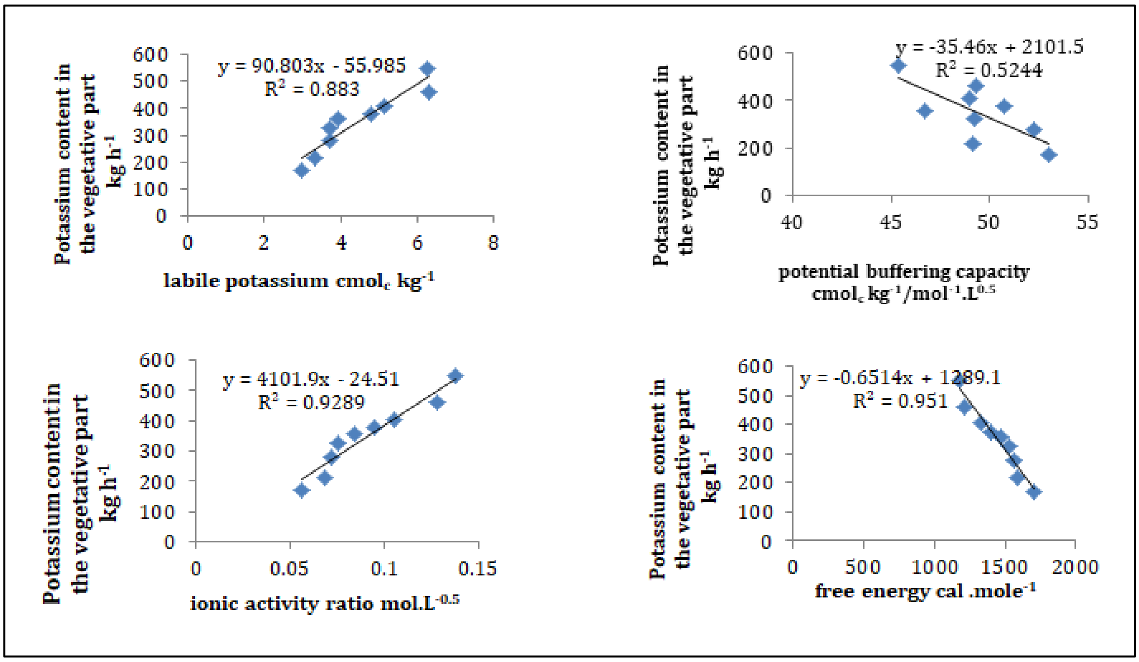

Figure 4. The relationship between thermodynamic parameters of potassium ion and dry matter yield in maize seeds.

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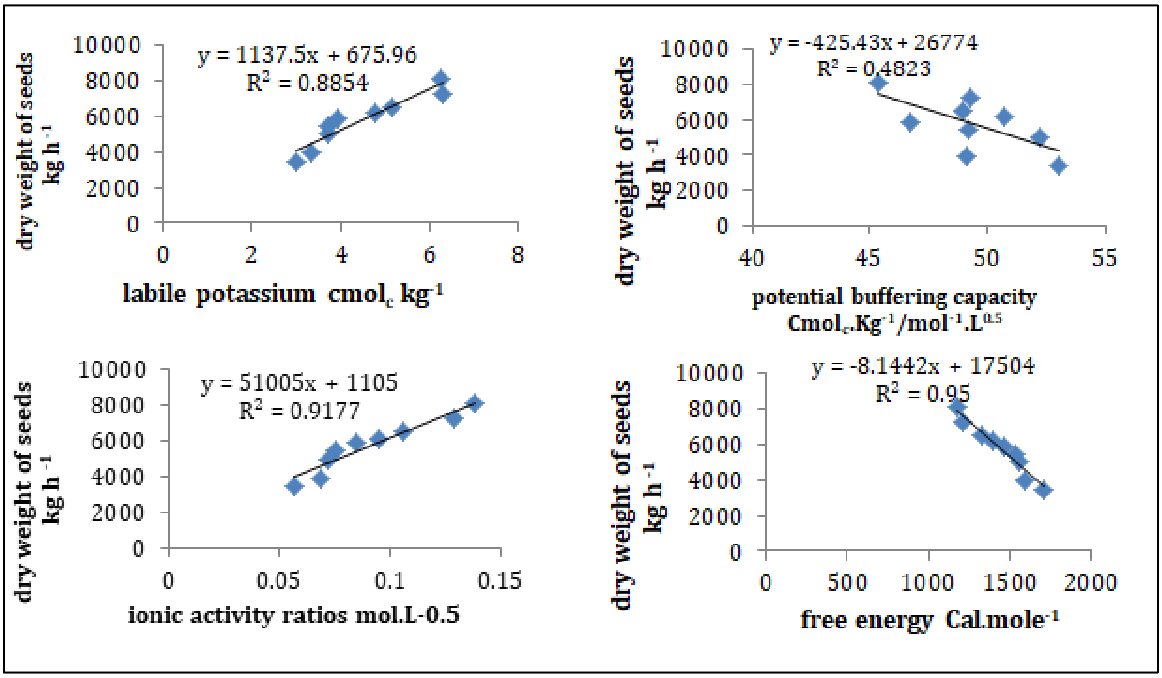

Figure 5. The relationship between the thermodynamic parameters of the potassium ion and the amount of potassium absorbed by the maize plant.

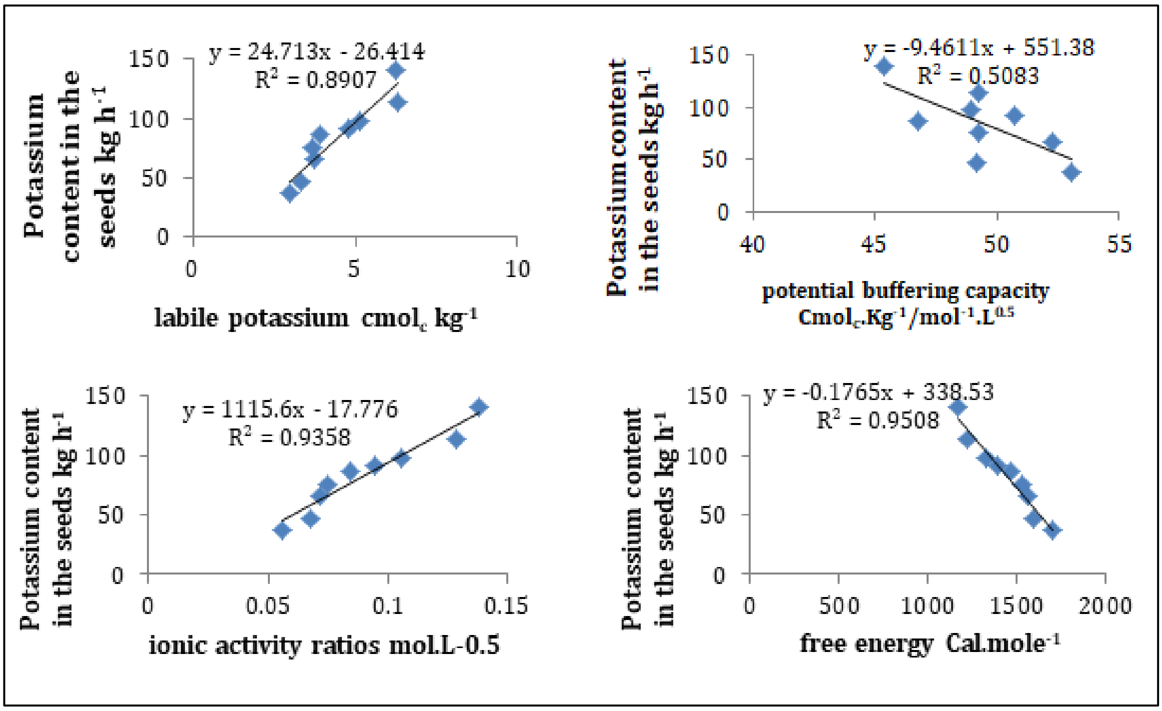

Figure 6. The relationship between thermodynamic parameters of potassium ion and the amount of potassium absorbed by maize seeds.

Conclusion

The ionic activity ratio ranged from (0.056 -0.141) mol. $L^{-0.5}$, labile potassium from (2.980-7.852) $Cmolc.kg^{-1}$, free energy from (-1705.371) cal. mole $kelvin^{-1}$ to (-1160.957) cal. mole $kelvin^{-1}$, and potential buffering capacity from (45.346 -55.737) $Cmolc.kg^{-1}/mol^{-1}.L^{0.5}$. The addition of mineral fertilizer and activated charcoal increased the dry weight of the vegetative part from (15816.29) kg h^{-1} to (31848.67) kg h^{-1} and the seed from (3455.83) kg h^{-1} to (8092.50) kg h^{-1}. Also, mineral fertilizer and activated charcoal increased the potassium content in the plant from (171.35) kg h^{-1} in the control treatment (F0B0) to (551.13) kg h^{-1} in the treatment (F2B2) and in the seeds from (37.45) kg h^{-1} to (140.03) kg h^{-1}.

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