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Article

Study the Effect of fulvic acid, humic acid and phosphate fertilizer on the kinetics and adsorption of phosphorous in calcareous soil

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Abstract: This study was conducted to evaluate the efficiency of fulvic and humic acids in the kinetics of phosphorus liberation and adsorption in calcareous soils, as they were added at levels of 20 and 40 kg.h^{-1} with three levels of phosphorus in the form of triple superphosphate fertilizer, 0, 50 and 100 kg. h^{-1}, the five kinematic equations were used which are the zero order equation, the first order equation, the exponential function equation, the diffusion equation and the Eloveg equation. The results showed the superiority of the exponential function equation, as it gave the highest values of the determination coefficient R2 was 0.953 and the lowest standard error value SEe amounted to 0.0584 and the superiority of fulvic acid over humic acid in increasing the speed of release of the added phosphorous at both levels and with an increase rate of 72.0, 45.5 and 25.0% at Level 20 kg.ha^{-1}, 41.2, 7.1 and 19.7% at the level of 40 kg.ha-1 And the levels of added phosphorous were 0, 50 and 100 kg h^{-1}, respectively, and the results showed in the adsorption experiment that the type of acid had an effect on the values of binding energy k and maximum adsorption Xm, as fulvic acid outperformed humic acid in reducing them and the percentage of decrease in energy values was Binding 38.7, 41.5 and 52.2%. As for the maximum adsorption values, the percentage of decrease was 44.2, 46.2 and 44.7%. An increase in the maximum adsorption values with time was also observed, as they were 1714, 2075 and 2083 µgP.gm^{-1} soil. The average binding energy values were 1.55 and 1.83 and 2.34 µg P.gm^{-1} in the case of humic, while in the case of Volvic, the maximum adsorption values were 955.5, 1079.5 and 1151.5 µg P.gm^{-1} in soil, while the binding energy values were 0.95, 1.07 and 1.11 ml. µg P^{-1} during three time periods. of adding both acids to the soil are 20, 60 and 100 days, respectively.

Keyword: humic acid; kinetics; fertilizer; superphosphate.

1. Introduction

Phosphorous is one of the basic and necessary nutrients, and it is called the key to life for its direct role in most of the basic biological processes within the plant and other living organisms in general, which cannot take place without it.[1].The chemistry of phosphorus in the soil is a complex matter because phosphorus is linked with many different compounds by a group of different bonds such as carbonate minerals, iron and aluminum oxides, in addition to its direct interaction with dissolved and exchanged ions and transforming it into a non-absorbable formula from the plant [2]. Phosphorous in Iraqi soil suffers from major problems in readiness Due to the increase in the soil content of carbonate minerals and the predominance of calcium ion in the equilibrium medium, as well as the increase in the interaction of the soil, which greatly contributes to the decrease in its availability [3]. Several attempts have been made to improve the availability of phosphorus in the soil by adding organic matter and agricultural sulfur and using phosphate gypsum and phosphate rock as a source of phosphorous element, in addition to the role of these materials in affecting other soil properties such as reducing soil interaction. Studies that have been conducted to its essential role in improving the availability of nutrients in the soil in addition to considering it as an organic reformer in salt-affected soils because of its role in chelating salt-effect ions such as sodium Calcium and magnesium when their concentration is increased in the equilibrium medium through the active groups in them represented by the carboxylic and phenolic groups[4] .The study conducted by [5] and [6] showed that fulvic and humic acids differ from each other in many properties, starting from the formal properties such as optical density E600/E400, molecular weight, content of carboxylic and phenolic groups, proportion of elements Such as carbon, oxygen, hydrogen, total acidity, aliphatic groups and aromatic groups.From the above it is clear that the behavior and effectiveness of these two acids in the soil are completely different according to the aforementioned properties and to know the effect and behavior of each of these acids in the soil in detail, this study was conducted to compare the efficiency of fulvic and humic acid in kinetics Phosphorous liberation and adsorption in calcareous soil.

2. Materials and methods

A biological experiment was carried out in calcareous soil with a silty mixture texture in one of the fields belonging to the College of Agricultural Engineering Sciences at the University of Baghdad, and its characteristics are shown in Table 1), which shows some of the physical and chemical properties in it and which were estimated according to what was mentioned in [7] a factorial experiment was carried out according to the design of randomized complete sectors. The first factor included three levels of phosphorus, which are 0, 50 and 100 kg p.h-1 in the form of triple superphosphate (20% P), and the second factor is represented by five Levels which are two types of humic and fulvic humic acids with two levels of addition to them (20 and 40) kg H^{-1} with the comparison treatment with three replicates so that the total of the experimental units is 45 experimental units. And the soil moisture content was maintained at the limits of the field capacity throughout the experiment period. Soil samples were taken from each experimental unit after 20, 40, 60, 80 and 100 days to study the kinetics and release of phosphorus in the soil over time. Dissolved phosphorous was extracted using % citric acid. 1 During, mathematical equations with empirical foundations and others based on kinetic chemistry were used, and referred to by [8] . These equations are:

1. Zero order equation (Ct) = C0 – Kdt – C0)
2. First order equation (C0- Ct) = ln C0 - Kdt)
3. Diffusion equation Ct/C0 = C0 - Kdt1/2
4. Ilvege equation Ct = C0 + Kd Lnt
5. Exponential function Ln Ct = Ln Ct + Kd Lnt

It represents:

C0 = the amount of phosphorous at time zero (mg.kg-1).

Ct = the amount of phosphorous released at time t (mg.kg-1).

Kd = rate of release rate (constant rate of release) (mg.kg-1.day-1).

t = time (day)

In order to determine the most efficient mathematical equation from the previous equations, the process of liberating phosphorous is described, the following indicators are adopted:

coefficient of determination (R2) and the value of Standard Error of Estimate (SEe).

The adsorption of phosphorous was also studied through the isothermal adsorption experiment, placing 5 gm of sieved soil with a sieve with holes diameter of 2 mm in a centrifuge tube with a capacity of 100 ml of treatments added to humic acids (humic or fulvic) only (CP_0, H_{20} P_0, H_{40} P_0, F_{20} P_0, F_{40} P_0). for the periods of time (100, 60, 20) days after adding the fertilizer, then adding to it concentrations of phosphorous are 0, 25, 50, 75 and 100 micrograms P ml^{-1} in the form of a solution of monopotassium phosphate (KH2PO4) in a volume of 50 ml and left for 24 hours, then agitated for a period Two hours, then it was placed in a centrifuge (2500 cycle min^{-1}) for 10 minutes to separate the clear solution from the soil, then the samples were filtered and the amount of phosphorus adsorbed was calculated by subtracting the concentration of phosphorous present in the filtrate from the added phosphorus. The relationship between the adsorbed phosphorous and phosphorous in the equilibrium solution was described using the equation Lankmire with one surface, as the values of binding energy ((k and maximum adsorption capacity Xm)) were calculated using the following linear formula: C/X = 1/kXm + C/Xm

Since:

X : concentration of phosphorus adsorbed μg pg^{-1} soil

C: the concentration of phosphorous in the equilibrium solution μg P mL^{-1}

k: binding energy in milliliters. micrograms P^{-1}

Xm: maximum adsorption μg Pg^{-1} in soil.

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

Traits		value	Measurement value
pH		7.60	---
$(EC)_e$		3.20	DC Siemens M^{-1}
CEC		17.53	Centimol kg^{-1} . shipment
Organic matter		9.1	gm. kg^{-1}
Carbonate metals		230.8	
ions dissolved in solution the soil	Ca^{++}	8.14	mmol $liter^{-1}$
	Mg^{++}	6.08	
	Na^{+}	2.34	
	K^{+}	0.53	
	Cl^{-}	18.28	
	HCO_3^{-}	10.41	
	SO_4^{--}	1.32	
ready-made nitrogen		27.3	$mg.kg^{-1}$ soil
ready-made phosphorous		4.80	
ready-made potassium		103.2	
bulk density		1.31	Mgm^{-3}
true density		2.63	Mgm^{-3}
porosity		0.455	%
Soil Separators	sand	231.00	gm kg^{-1} soil
	mud	200.00	
	silt	569.00	
tissue		Silty Loam	----
Volumetric moisture content at 33 kPa		0.391	$cm^{-3}.cm^{-3}$
Volumetric moisture content at 1500 kPa		0.173	$cm^{-3}.cm^{-3}$
ready water		0.218	

3. Results

3.1. Kinetics of phosphorous release in soil

The results shown in Table (2) show the results of the five kinetic equations used to describe the kinetics of phosphorous in soil, which are the zero-order equation, the first-order equation, the diffusion equation, the exponential function, and the Eloveg equation, as the equations were compared based on the values of the coefficient of determination (R2 and the estimated standard error (SEe) by taking the highest value of the coefficient of determination and the lowest value of the standard error, and the results showed that the equation of the exponential function is superior to the rest of the equations as it gave the lowest value of the standard error of 0.0584495 and the highest value of the coefficient of determination 0.9534. The high values of the coefficient of determination in the Eloveg equation, which amounted to 0.9642, but the value of the standard error of it was large, as it reached 3.84, and thus the exponential function model is the best In describing the liberable phosphorous from the levels of added fertilizer and under the influence of different levels of fulvic and humic acids with time, the kinetic equations graded in describing the release of phosphorus with time depending on the coefficient of determination and the standard error as follows:

Power < first order < Elovege < Rank Zero < Diffusion .

The regression coefficient values were 0.9534, 0.9284, 0.9642, 0.8813 and 0.9302, while the standard error values were 0.0584495, 0.153207, 3.844957, 0.360271 and 6.32039437, respectively.

The superiority of the exponential function equation in describing the liberation of phosphorous from the soil indicates that the liberated amount of phosphorous is proportional to time and that the process of liberation of orthophosphate ions is determined by the effect of additives that interact in the soil with time, thus affecting the increase in the capacity of liberation [8,9,10]

Table 2. values of the coefficient of determination R2 and the standard error SEe for the kinematics equations used in this study

Treatments	Zero		Firest		Power		Elovich		Diffusion	
	SE	R2	SE	R2	SE	R2	SE	R2	SE	R2
C P0	0.271959	0.8099	0.139796	0.8781	0.131475	0.9042	2.890741	0.9438	1.04363698	0.8845
C P1	0.364308	0.815	0.16024	0.8917	0.111836	0.9044	2.857033	0.935	2.43330032	0.8822
C P2	0.329973	0.8634	0.12097	0.9383	0.095891	0.9341	3.518948	0.9649	2.09122646	0.9229
H20 P0	0.247835	0.882	0.123125	0.9287	0.079575	0.963	3.629166	0.9825	0.93487651	0.9441
H20 P1	0.250339	0.8176	0.542144	0.7293	0.080361	0.8797	1.991233	0.901	8.460142	0.8212
H20 P2	0.563613	0.766	0.221394	0.8692	0.069614	0.8988	2.912163	0.9206	10.1780091	0.8501
H40 P0	0.317333	0.893	0.116235	0.9547	0.058479	0.9707	3.396863	0.9889	2.73927591	0.9525
H40 P1	0.431764	0.9067	0.150263	0.9571	0.030437	0.9824	1.17102	0.9874	10.0434994	0.9596
H40 P2	0.463055	0.8862	0.133418	0.9628	0.035465	0.9744	2.010657	0.9866	10.6822656	0.9476
F20 P0	0.115672	0.9907	0.035998	0.9963	0.0028127	0.9962	7.424501	0.9752	0.18262457	0.997
F20 P1	0.306729	0.9693	0.059707	0.9936	0.014678	0.9974	3.75637	0.9945	7.086666	0.9944
F20 P2	0.521289	0.8545	0.153055	0.9487	0.041993	0.9586	3.719438	0.9743	12.361631	0.9243
F40 P0	0.271961	0.9784	0.105746	0.9512	0.062445	0.9871	13.37634	0.9424	2.4522057	0.9724
F40 P1	0.533816	0.849	0.176931	0.9324	0.042887	0.957	3.701395	0.9698	12.3679762	0.9197
F40 P2	0.414415	0.9382	0.059087	0.994	0.018794	0.9932	1.318498	0.9964	11.7488769	0.9801
Average	0.360271	0.8813	0.153207	0.9284	0.0584495	0.9534	3.844957	0.9642	6.32039437	0.9302

[1] Since: C: comparison level without adding humic acids
[2] H20: Humic acid at a level of 20 kg.H^{-1}
[3] H40: Humic acid level 40 kg.H^{-1}
[4] F20: fulvic acid level 20 kg.h^{-1}
[5] F40: fulvic acid level 40 kg.h^{-1}
[6] Po= 0kg p.h^{-1}, triple superphosphate (20% P)
[7] P1 = 50 Kg p.h^{-1} triple superphosphate (20% P)
[8] P2 = 100 kg p.h^{-1} triple superphosphate (20% P)

The results shown in Figures 1 and 2 also showed the speed of phosphorus release over time, as the results showed that the addition of fulvic and humic acids had a significant impact on increasing the speed of phosphorous release with time in the soil, as the rate of release speed was 0.308, 0.704, 0.723, 0.442 and 0.723 and 0.812 mg. kg. Day-1 at phosphorous levels P0, P1 and P2, respectively when adding fulvic acid, while when adding humic acid, the rate of release was 0.179, 0.484, 0.578, 0.313, 0.675 and 0.678 mg. kg. Day-1 at phosphorous levels P0, P1 and P2, respectively, and for acid levels of 20 and 40 kgH-1.

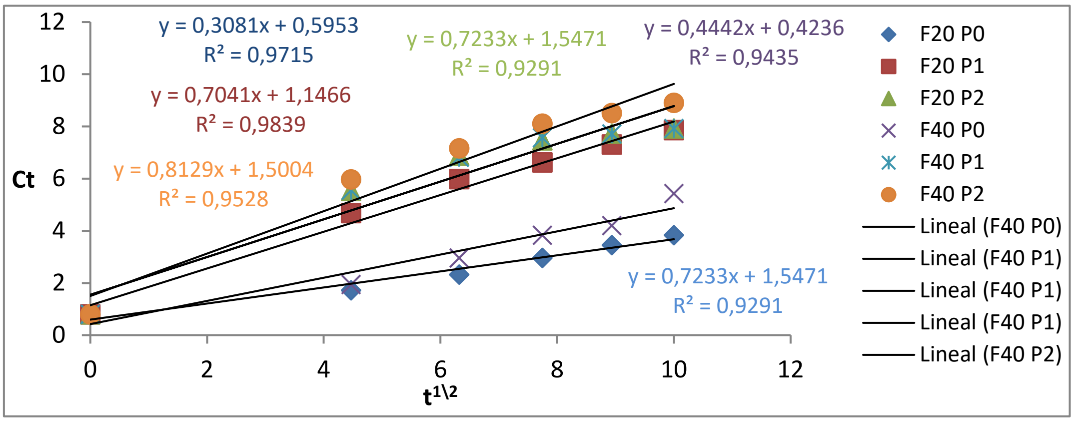

Figure 1. The relationship between the concentration of phosphorous released with time in humic acid treatments

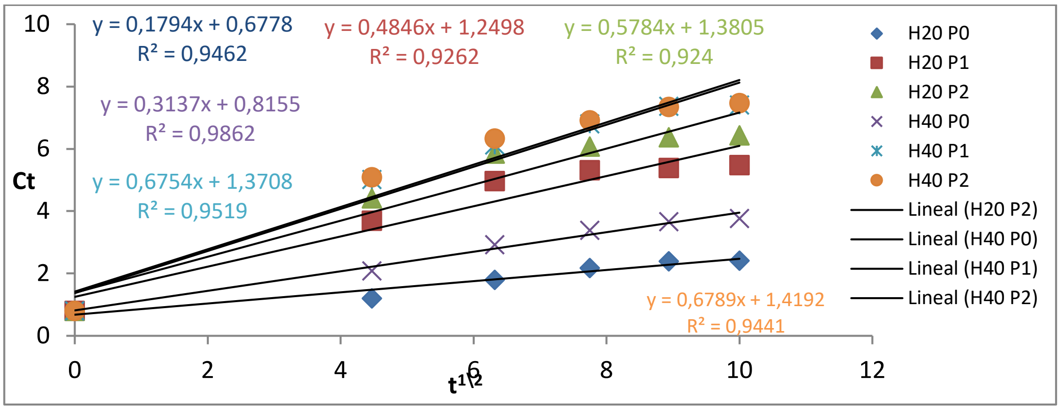

Figure 2. The relationship between the concentration of liberated phosphorous with time in fulvic acid treatments

The results shown in the figures showed the superiority of fulvic acid over humic acid in increasing the speed of release of phosphorous added to the soil with time and at both levels 20 and 40 kg H-1, as the percentage of increase was 72.0, 45.5 and 25.0% at phosphorous levels P0, P1 and P2, respectively, at the level of 20 kg H-1. As for the addition level of 40 kg H-1, the percentage of fulvic acid over humic is 41.2, 7.1 and 19.7% at phosphorous levels P0, P1 and P2, respectively, and the superiority of fulvic acid over humic acid is attributed to Increasing the speed of liberation of phosphorous added to the characteristics that distinguish fulvic acid compared to humic acid, such as lower molecular weight, which makes its disintegration in the soil faster, as well as an increase in the total acidity in addition to an increase in the percentage of phenolic aggregates and an increase in the proportion of aromatic compounds compared to aliphatic compounds, and this was confirmed by[11,12,4] who indicated that the difference in the nature of the chemical composition of fulvic acid and humic has a significant impact on the availability of phosphorus in the soil.

3.2. Experiment with isothermic adsorption of phosphorous

For the purpose of evaluating the effect of the type and level of fulvic and humic acids on the adsorption of phosphorus in the soil during three different phases of time 20, 60 and 100 days, the Lancmeyer equation of one surface was used and the values of the binding energy k and the maximum adsorption capacity Xm were extracted and the results shown in the table (3) And Figures (3-17) that fulvic and humic acid had a significant effect on reducing the binding energy values of phosphorous compared to the treatment that did not add any of the acids to it, as the percentage of decrease was 43.6, 65.4, 44.5, 67.5, 30.5 and 67.0% for acid Humic and fulvic acids during the three phases are 20, 40 and 100 days, respectively. It was also observed that the maximum adsorption values decreased when adding humic and fulvic acids if the percentage of decrease reached 43.4, 68.4, 39.7, 67.6, 43.7 and 68.9% for fulvic and humic acids during the three phases. 20, 60 and 100 days, respectively, and the reason for this is due to the effect of the two acids In reducing the values of the degree of reaction, which contributes to increasing the availability of phosphorus, in addition to the role that these acids play in reducing the fixation of phosphorus in the soil by restricting the movement of ions that have a negative effect on the readiness of calcium and magnesium through the chelation and restriction process carried out by the effective groups represented with carboxylic and phenolic groups, and this is consistent with what he referred to [13,4] .

Table 3. The effect of the type and level of fulvic and humic acid on the values of binding energy (mol. µg P-1) and maximum adsorption capacity (µg P. g^{-1} soil)

time)day(**Treatment**	**20**		**60**		**100**	
	Xm	k	Xm	k	Xm	k
CP0	3030	2.75	3333	3.30	3704	3.37
H20 P0	2000	1.79	2500	2.00	2500	2.86
H40 P0	1428	1.30	1515	1.65	1666	1.82
F20 P0	1111	1.12	1250	1.30	1351	1.35
F40 P0	800	0.78	909	0.85	952	0.88

As for the effect of the addition levels of humic and fulvic acids on the binding energy values and adsorption capacity, it was observed that the addition level of 40 kg H-1 exceeded the addition level of 20 kg H-1 in reducing the binding energy values, as the percentage of decrease in humic acid reached 27.3 and 17.5 And 36.3% in fulvic acid, 30.3, 34.6, and 34.8 percent. As for the decrease in the values of the greatest adsorption capacity when the level of humic acid was increased to 40 kg H-1, it reached 28.6, 39.4 and 33.3%. The greatest adsorption was 27.9, 27.2, and 29.5% during the three growth stages of 20, 60 and 100 days, respectively, and the reason for the decrease in the values of the binding energy and the greatest adsorption with the increase in adding the level of both acids to the effect of both acids in decreasing the values of the soil reaction number and increasing the proportion of Active groups represented by carboxyl and phenolic groups and their role And its role in reducing the impact of negatively affected ions on the readiness of phosphorous such as calcium through the process of chelation and complexity in addition to its role in reducing the values of the degree of interaction of the equilibrium medium, which makes orthophosphate ions more ready in the soil.

In general, it was observed that the adsorption values and binding energy increased with the growth stages of 20, 60 and 100 days, and at the addition level of 20 kg H-1 compared to the level of 40 kg H-1 and for both acids, it was greater in the case of humic acid than fulvic acid, as it reached The average adsorption capacity of the greatest in the case of humic is 1714, 2075 and 2083 µg P gm-1 soil, while in the case of fulvic 955.5, 1079.5 and 1151.5 µg P g-1 soil, while the average values of binding energy in adding humic acid are 1.55, 1.83 and 2.34 ml. Microgram-1 P and when adding fulvic, it reached 0.95 and 1079.55 and 1.11 ml. Microgram-1 P during the growth stages of 20, 60 and 100 days, respectively. The increase in the binding and adsorption energy with time is due to the decrease in the effect of acids in the effect on the availability of phosphorous and its exposure to the adsorption process, which develops to a precipitation state with time and this agrees With what was found [1,9] which indicated the role of time in keeping phosphorous ready in the soil, so we conclude that adding these acids with the stages of growth is better to maintain the readiness of phosphorus in the soil.

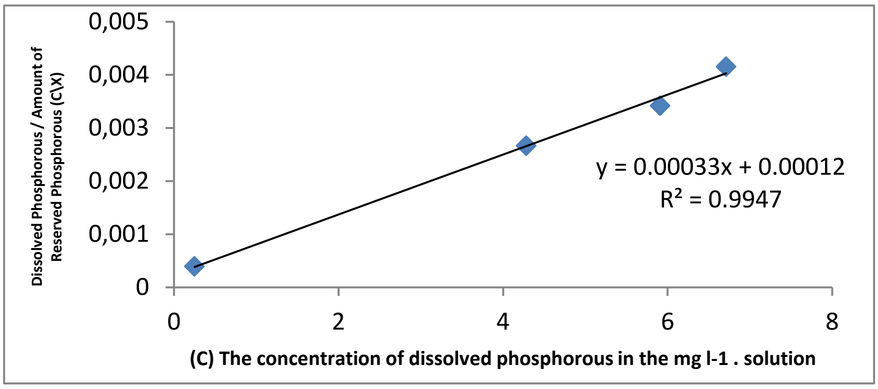

Figure 3. The relationship between the phosphorous concentration in the equilibrium solution (C) and the values (C\X) of the comparison treatment CP0 at the time of 20 days

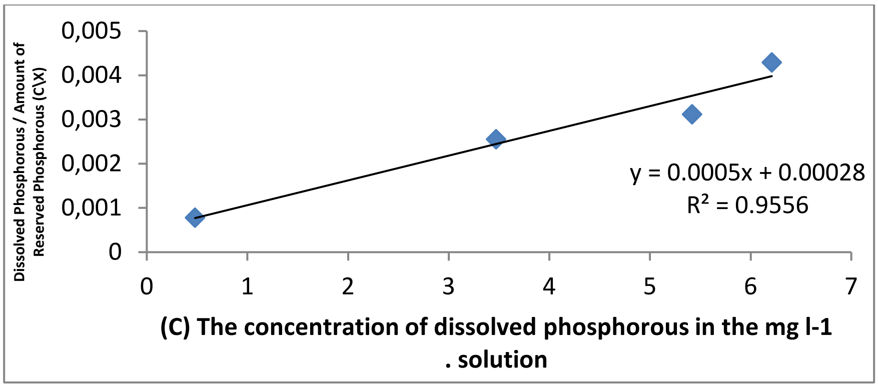

Figure 4. The relationship between the phosphorous concentration in the equilibrium solution (C) and the values (C\X) of the treatment H20P0 at the time of 20 days

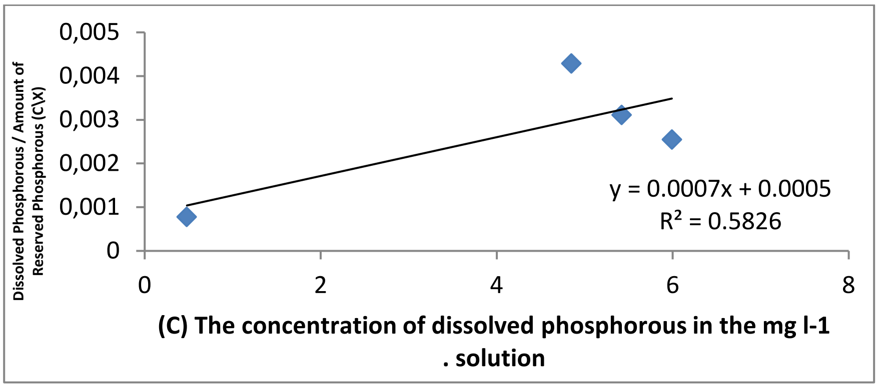

Figure 5. The relationship between the concentration of phosphorous in equilibrium solution (C) and values (C\X) of treatment H40P0 at the time of 20 days

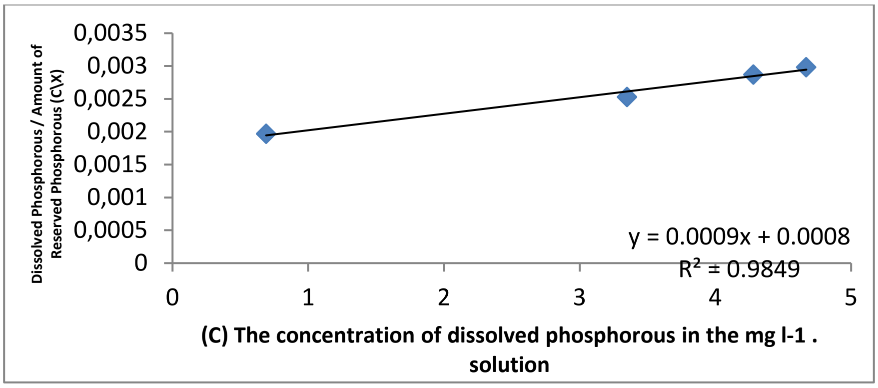

Figure 6. The relationship between the concentration of phosphorous in equilibrium solution (C) and values (C\X) of treatment F20P0 at the time of 20 days

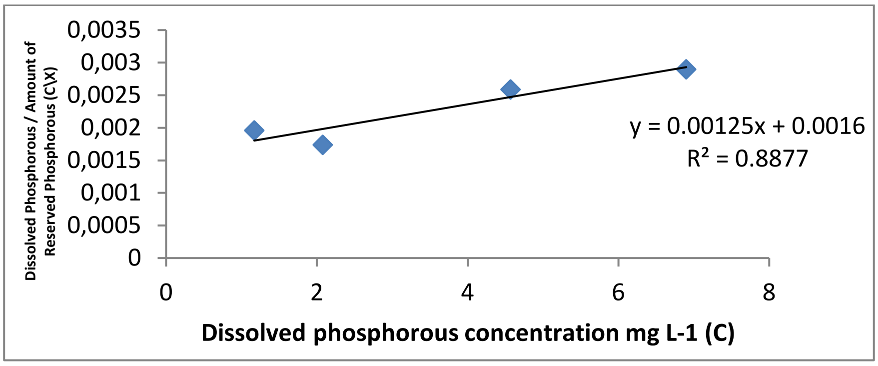

Figure 7. The relationship between the concentration of phosphorous in equilibrium solution (C) and values (C\X) of treatment F40P0 at the time of 20 days

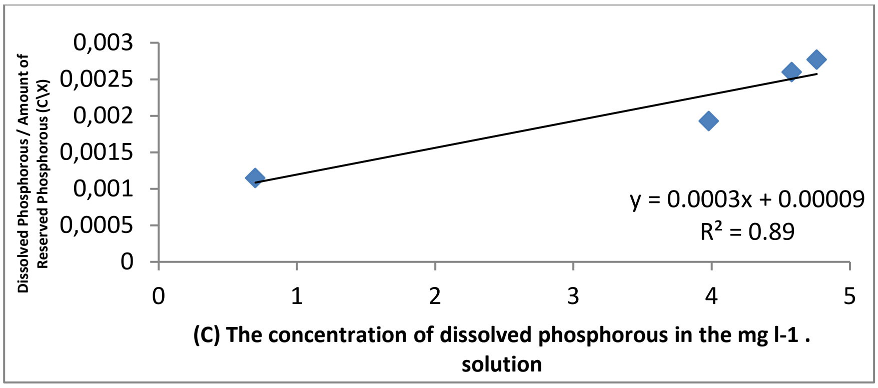

Figure 8. The relationship between phosphorous concentration in equilibrium solution (C) and values (C/X) of treatment CP0 at the time of 60 days

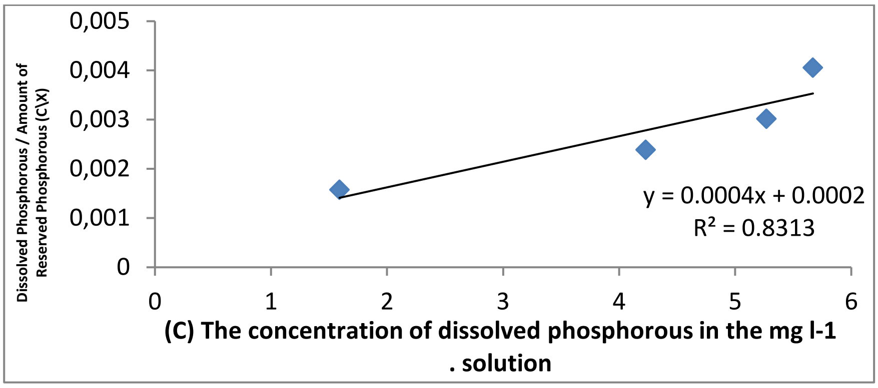

Figure 9. For a relationship between the concentration of phosphorous in equilibrium solution (C) and values (C\X) of treatment H20P0 at the time of 60 days

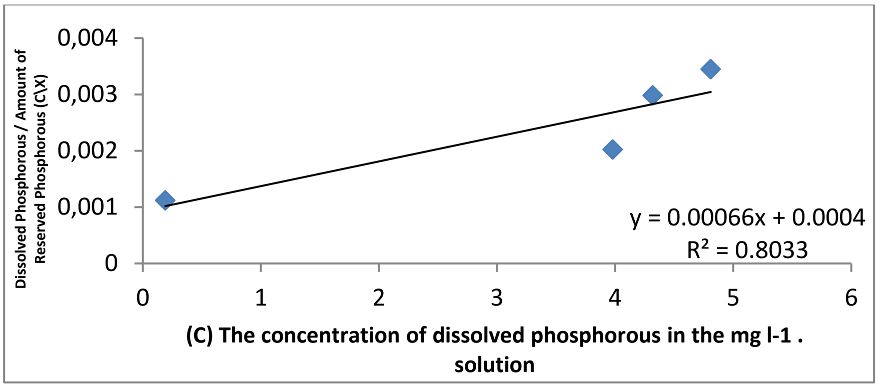

Figure 10. The relationship between the concentration of phosphorous in equilibrium solution (C) and values (C\X) of treatment H40P0 at the time of 60 days

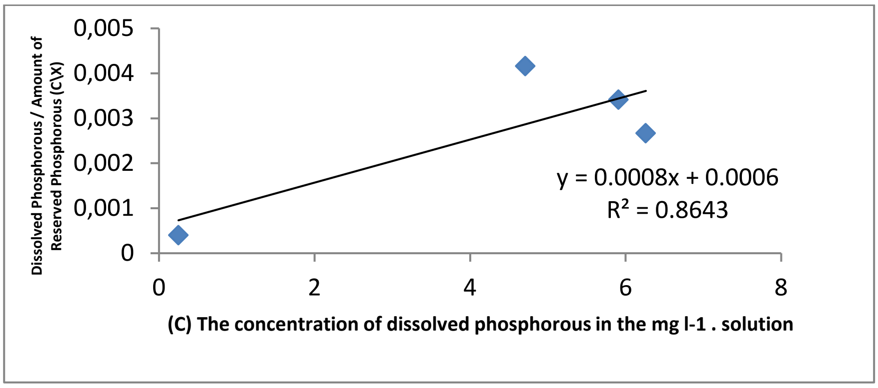

Figure 11. The relationship between the concentration of phosphorous in equilibrium solution (C) and values (C\X) of treatment F20P0 at the time of 60 days

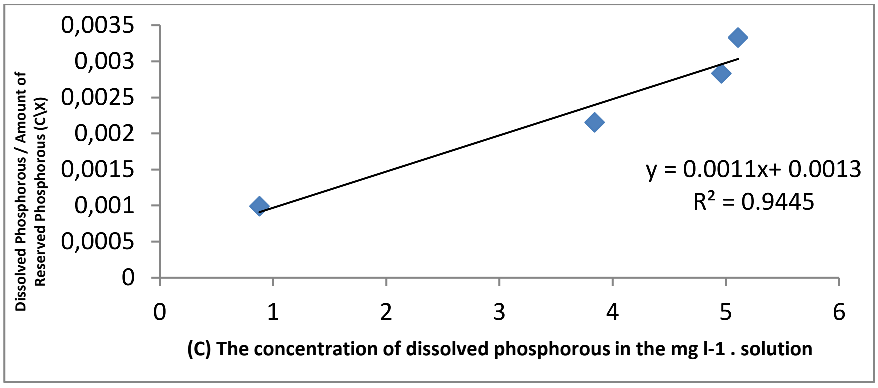

Figure 12. For a relationship between the concentration of phosphorous in equilibrium solution (C) and values (C\X) of treatment F40P0 at the time of 60 days

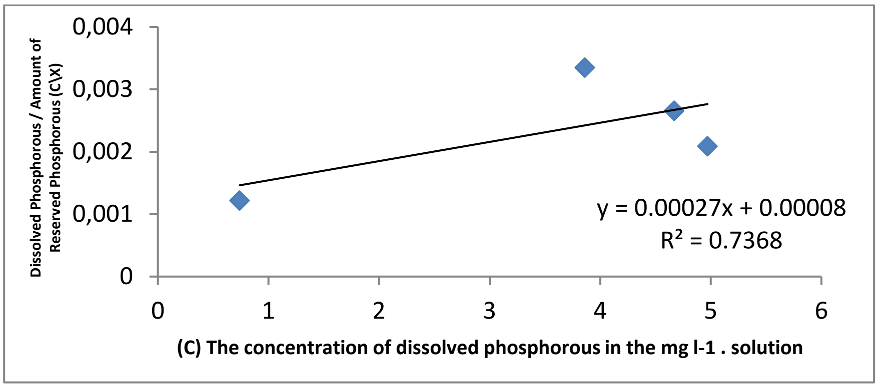

Figure 13. The relationship between the phosphorous concentration in the equilibrium solution (C) and the values (C/X) of the comparison treatment CP0 at the time of 100 days.

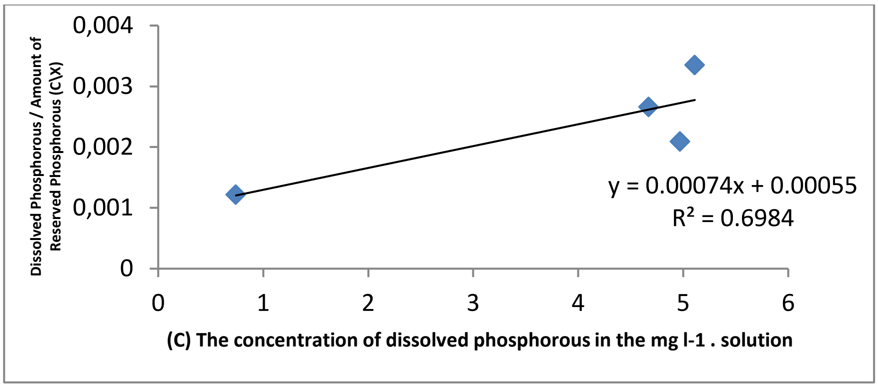

Figure 14. The relationship between the concentration of phosphorous in equilibrium solution (C) and values (C\X) of treatment H20P0 at the time of 100 days

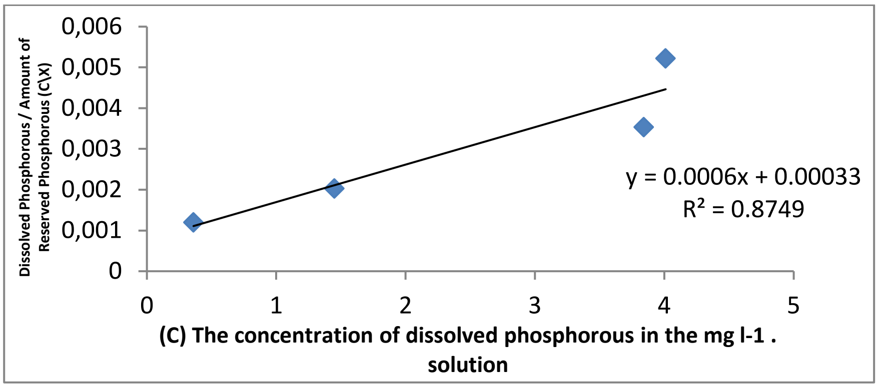

Figure 15. The relationship between the concentration of phosphorous in equilibrium solution (C) and values (C\X) of treatment H40P0 at the time of 100 days

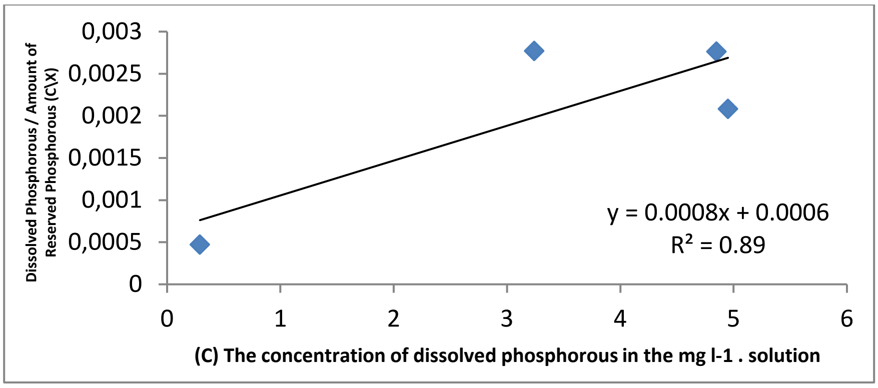

Figure 16. The relationship between the concentration of phosphorous in equilibrium solution (C) and values (C\X) of the treatment F20P0 at the time of 100 days

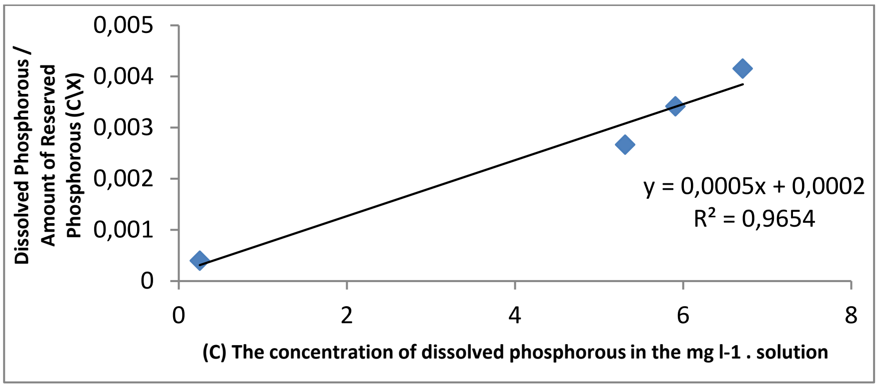

Figure 17. The relationship between the concentration of phosphorous in equilibrium solution (C) and values (C\X) of treatment F40P0 at the time of 100 days

As for the effect of the type of humic acid on the values of binding energy and maximum adsorption, the results showed the superiority of fulvic acid over humic acid in reducing binding energy values during the growth stages, as the percentage decrease reached 38.7, 41.5 and 52.2% for the stages of 20, 60 and 100 days, respectively. As for the maximum adsorption values, a decrease in their values was observed in the presence of fulvic acid compared to humic acid, as the percentage of decrease was 44.2, 46.2 and 44.7% during the stages of 20, 60 and 100 days, respectively

4.Discussion

The results can be attributed tothe decrease in the values of binding energy and adsorption capacity The presence of fulvic acid compared to humic acid to the characteristics that distinguish it, such as higher values of total acidity and an increase in the proportion of aromatic compounds compared to the aromatic compounds as well as lower values of molecular weight, which make it a compound that decomposes faster compared to humic acid, which is characterized by lower values of total acidity and an increase in the proportion of compounds Elasticity and an increase in the molecular weight of this acid, which reaches 100,000 daltons, and this is confirmed [14,6].

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