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UTILIZATION OF RICE HUSK IN THE SORPTION OF EUTROPHICATION NITROGEN AND PRODUCING A USEFUL ORGANIC FERTILIZER FOR PLANT PRODUCTION

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Abstract: In the present research, the optimum exploitation procedure of the agricultural waste was conducted reaching to zero residue level (ZRL). This aim was fulfilled via two steps. The first one was the removing of nitrogen from simulated synthetic aqueous solutions (SSAS) by using an agricultural waste (which is Iraqi rice husk, IRH)) as a bio sorbent material in a fixed bed continuous mode and under many multi operating conditions; which were concentration, pH, flow rate, contact time, temperature and height of adsorbent material in the fixed bed. The second step was the utilization of the adsorption residue, which is affluent with adsorbed loaded nitrogen, by mixing it with agriculture soil as a low cost compost for tomato harvest. The results show that the removal efficiency of nitrogen was decreased with increasing N concentration, pH and flowrate but increased with increasing the contact time, temperature and height of adsorbent material in the fixed bed. The maximum percentage adsorption efficiency was 96.74%. The adsorption residue exhibited a good behavior when used as manure and the weight of tomatoes was increased by 18.25%, compared with the same harvest produced without using this fertilizer. Thus it can be profiting from the agricultural waste by a simple, economic and eco-friendly method accessing to ZRL.

Keywords: *eutrophication, adsorption, nitrogen, rice husk, ZRL and SSAS*

إستخدام قشور الرز في إمتصاص النيتروجين المسبب للإثراء الغذائي وإنتاج سماد عضوي مفيد للإنتاج النباتي

الخلاصة: في هذا البحث ، تم إنجاز طريقة الإستفادة المثلى من المخلفات الزراعية وصولا إلى مستوى المتبقيات الصفرية (ZRL) . تحقق الهدف أعلاه من خلال خطوتين . الخطوة الأولى كانت إزالة النتروجين من المحاليل المائية المصنعة (SSAS) بإستخدام أحد انواع المخلفات الزراعية (وهي قشور الرز العراقية (IRH)) كمادة مازة حيوية في منظومة العمود المحشو ذات النظام المستمر الجريان وتحت ظروف تشغيلية متعددة وهي : التركيز ، الدالة الحامضية ، ومعدّل الجريان ، وزمن الإستبقاء ، ودرجة الحرارة ، وإرتفاع طبقة المادة المازة في العمود المحشو . الخطوة الثانية كانت الإستفادة من متبقيات الإمتزاز والتي كانت محملة بالنتروجين الممتز من خلال خلطها (مزجها) مع التربة الزراعية المستخدمة في إنتاج محصول الطماطة كسماد رخيص الثمن . بينت النتائج المستحصلة أن أعلى كفاءة لإزالة النتروجين بإستخدام قشور الرز وصلت إلى 96.74%، وأنها كانت تتناقص بزيادة تركيز N والدالة الحامضية ومعدل الجريان ولكنّها تتزايد بزيادة زمن الإستبقاء ودرجة الحرارة وإرتفاع طبقة المادة المازة في العمود المحشو . كما أظهرت متبقيات الإمتزاز سلوكاً جيداً عند إستخدامها كسماد عضوي وأدّت إلى زيادة وزن محصول الطماطة بنسبة 18.25% مقارنة مع المحصول المنتج بدون إستخدام هذه المتبقيات كسماد . وبهذا أصبح بالإمكان الإستفادة من المخلفات الزراعية بطريقة بسيطة وإقتصادية وصديقة للبيئة وصولاً إلى مستوى المتبقيات الصفرية (ZRL) .

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1. Introduction

The environment is suffering from many and endless problems represented by dwindling of resource, climate change, ozone layer depletion, acid rains, desertification etc. For the time being, perhaps the most prominent and important issues confronting the environment, linked directly or indirectly with all other environmental troubles and their impacts have been dramatically aggravated to the extent that become threaten human life, it is the environmental pollution [1]. In general the environmental pollution can be defined as any change happens in one or more of components (living or non-living) that commonplace located in a detected eco-system (whether natural or artificial) as a result of a deliberate input or inadvertently entry or side byproduct of one or more substances basically neither existent within the ecosystem nor classified as a part of it which leading to variation (intensify or diminution) or get disorder or negative effect temporary or permanent damage in any authentically components of ecosystem or resulting in disruption of ecological balancing existing among known components of the ecosystem [2]. It could be restricted the causes of environmental pollution by two main reasons: the first one is naturally due to natural disasters such as dust storms, thunderbolt, earthquakes, flooding, volcanoes, soil erosion, and devastating hurricanes, while the other reason occurs by human due to industrial, agricultural, military, recreational and scientific actions and the uses of modern technique manifestations and developed innovations like various electronic devices [3].

Both types of environmental pollution cause adverse effects on human whether on health side or on psycological and neural aspect. Not only that just, but the animals and plants also affected by the pollution as well as the terrifying effects that occur the environment itself. Agriculture is considered as one of the oldest and most important activities carried out by the human since his presence on the earth, close to its association with his life and his survival [4]. As a result of increasing and continued population growth in the world year after year, the demand for food has increased and due to the limitation and continuously decreasing of agricultural land area for the construction of infrastructure, service residential and entertainment facilities to meet the diverse and growing human requirements, the use of fertilizers with various kinds and quantities are increased too to raise the fertility of the agricultural soil thereby increasing the agricultural production [5].

The eutrophication means in simple a rise in the concentration of basic substances for plants feeding represented by nitrogen and phosphorus compounds in narrow and shallow seawater, artificial lakes, dam lakes and reservoirs as a result of natural factors or throw an organic contaminants in it, such as sewage and the remains of agricultural fertilizers or other chemicals leading to rapid growth of algae and unnecessary plants that cause clear disruption with aquatic ecosystem, limit the penetrate sunlight arrival to depths of seas and oceans leading to the obstruction of the photosynthesis process and working on a lack of oxygen element required and necessary to support the life of aquatic organisms causing a sharp decrease in the number of fish and other neighborhoods or even drought Lakes sometimes in addition to send the petition of the foul and alienating smells and the sickening and unacceptable appearance as a result of rotting organic material floating on the surface of the water as well as it becomes an enabling environment for the breeding of insects, especially mosquitoes [6]. The presence of organic matter in the agricultural waste leads to decompose it biologically by microorganisms such as bacteria and wasted due to that decomposition a toxic gasses and liquid substances such as nitrogen oxides and sulfur oxides, which lead to contamination of surface soil, influencing on groundwater quality, and raise the proportion of the acids, making the soil unsuitable for germination.

The accumulated agricultural wastes may become an appropriate home and convenient environment for breeding, reproduction and growth of harmful insects, pests, rodents and vectors of epidemics and diseases such as mice, rats, cockroaches and flies [7]. Treatment of eutrophication is conducted by several methods such as mechanical, biological, bio-mechanical and chemical methods while the agricultural waste can be recycled to produce fodder and other useful materials [8].

In Iraq, most of fertilizers used in agriculture are the urea fertilizers i.e. an important source for nitrogen pollution for soil and water resources eventually. On the other hand, the rice husk is produced in Iraq with huge quantities which compose a problem to dispose it in suitable way. This paper show a novel way to address the eutrophication phenomenon in the water by nitrogen adsorption method using a well-known large quantities types of agricultural waste which is rice husks and then use the residues of nitrogen adsorption in the preparation of composts for the tomatoes crop. By this way it is handled two types of pollution and the production of useful material from the residues in a simple, low cost, economic and eco-friendly method accessing to Zero Residue Level (ZRL).

2. Materials and Methods

2.1. Preparation of Adsorbent Media (Iraqi Rice husk)

The source of the Iraqi rice husks (IRH) used in this study was the rice fields in Al-Shanafia sub-district (250 km south of Baghdad). The collected rice husk was firstly washed three times with doubled distilled water to remove any dust that stucked in it from the field, then was boiled with hot water for eliminating color and any fine impurities may be loaded on the rice husk which could not be removed by washing in the first step. Finally, the rice husk was dried at 105°C for overnight. Thus the rice husk become ready for adsorption process, doesn't require any further treatment and used in its veritable segment size.

The surface area of IRH was measured by BET (Brunauer–Emmett–Teller nitrogen adsorption technique). The physical properties of IRH were as follows: 17.5 m^2/g BET surface area, 0.5124 g/cm^3 bulk density and 0.38 porosity by fraction. The chemical composition of IRH was conducted too, and the ash analysis shows that it contains (SiO_2: 90.7; Al_2O_3: 0.13; Fe_2O_3: 0.06; TiO_2: 0.015; CaO: 0.61; MgO: 0.25; Na_2O: 0.09; K_2O: 2.64; P_2O_5: 0.73; Loss of Ignition, LOI: 4.71; all ratios are in % weight).

2.2. Stock Solution

The nitrogen solution used in this investigation was a simulated synthetic aqueous solution (SSAS) to eschewing any inconsistency or interference or influencing may be occurred with other substances when using real solutions contaminated with nitrogen. Preparation of nitrogen solutions were carried out through dissolving an appropriate amount of ammonium chloride (NH_4Cl) in 1 liter of distilled water to obtain a stock solution of 1000 mg/l at room temperature. Any solution of nitrogen used in any experiment was prepared by diluting the required amount of stock solution with distilled water to the desired concentration. Spectrophotometer was used to determine the concentration of total nitrogen in the treated solution at 493 nm using the method described in[9].

2.3. Continuous Packed Bed Unit Experiments

The removal process of nitrogen from contaminated SSAS was conducted by the adsorption process and using IRH as an adsorbent media via continuous packed beds unit as shown in Figure 1. This unit was consisting of plastic container for contaminated nitrogen solution (SSAS) of (5 liters) capacity and one packed bed column. The bed was 5 cm ID, 0.5 m height and packed with IRH adsorbent media to a height of 0.4m separated from top and bottom with small glass beads.

Adsorption column of continuous mode experiments were conducted in order to test the nitrogen removal by treated contaminated SSAS water at various bed heights of the adsorbent media (i.e. IRH) and different flow rates of SSAS of nitrogen. After the packed bed column accommodation and the required amount of adsorbent media was put, the treatment processes starts by allowing the nitrogen SSAS flow through the packed bed column from the container through the first pump at a precise flow rate in experiment, which is adjusted by the valve and rotameter as shown in Figure 1.

To determine the best operational conditions, the experiments were carried out at a temperature between (20–55°C), various pH values of (1–8), different initial nitrogen concentrations between (1–100) mg/l and at different flow rates (5–100 ml/min) for nitrogen initial feed concentration. Outlet treated samples were collected every 10 minutes from the bottom of column and the unadsorbed concentration of nitrogen in SSAS was analyzed and detected by spectrophotometer according to [9].

Figure1a.ContinuousPackedBedUnit (photograph)

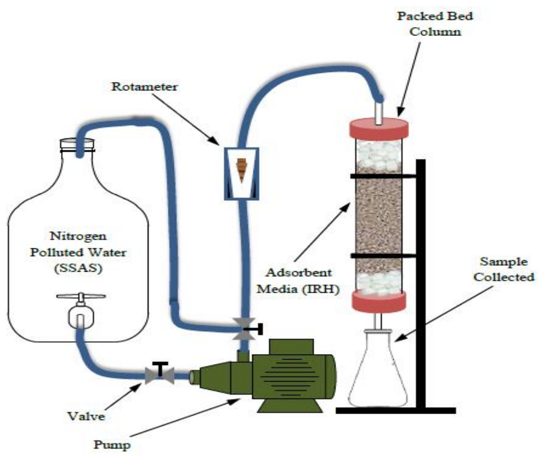

Figure 1b.Continuous Packed Bed Unit (Diagram)

3. Results and Discussions

3.1. Initial Concentration Effect

The initial concentration experiments were performed at varied concentration range between (1-100 mg/l) and keeping all other variables constant, as shown in Figure 2. The results show that the percentage removal of nitrogen from SSAS was increased with the decreasing of the nitrogen initial concentration and the maximum removal was reached to about 96.74% at a concentration of 1 mg/l. This result may be explained according to the active sites founded in the sorbent media IRH. When the height of adsorbent media was fixed the amount of IRH was fixed also, therefore the surface area and the number of active sites that responsible for adsorption was constant too. So, when the concentration of nitrogen in SSAS was increased this means the amount of nitrogen molecules was increasing too and these molecules were competed on these limited number of active sites. While when the concentration of nitrogen was low the same number of active sites attached with the same molecules but here the rest amount of nitrogen molecules was less than the first case. Thus, the percentage removal of nitrogen was increased when the concentration of nitrogen was decreased and vice versa. This result is agreement with [10].

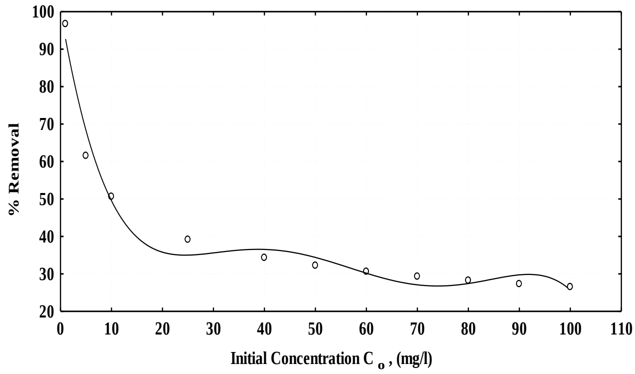

Figure 2. Effect of initial concentration ($C_{\circ}$) on the percent removal of nitrogen @ T_f =55°C, *l*= 0.4m, *pH*=1, *t*=60 min. and *F*=5 ml/min.

3.2. pH Effect

When all other parameters are fixed at optimum conditions, the experiments of SSAS pH effect were conducted at pH ranging between 1-8. The obtained results illustrate in Figure 3. The maximum removal efficiency was 96.74% at pH=1. It's obvious that the adsorption process is dependent predominantly on the hydronium ions concentration i.e. pH function. When the pH value was high, i.e. basic ambient, the concentration of hydroxide ions (OH^-) is high comparing with hydronium ions (H^+) in SSAS. So, the surface of sorbent media IRH charging with negative charge (according to abundance of hydroxide ions existing) and the repulsion force was constructed with the nitrogen ions in SSAS. While adverse effect was presenting at low values of pH, because the positive surface charge is attracting the negative nitrogen ions and attached physically with it in the active sites of sorbent media IRH. Therefore the percentage of nitrogen removal is increasing when the pH values of SSAS decrease. This result is in agreement with [11].

3.3. Adsorbent Media Bed Height Effect

The effect of height of adsorbent media column was determined depending on the results obtained from the practical experiments which carried out in the equal range between (0.1-0.4 m) of column and at constant the other operating conditions. The maximum removal efficiency was 96.74% at l =0.4 m.The result of this factor indicates that there is a direct correlation between the percentage removal and the bed length, i.e. when the height of adsorbent media is increased the percentage removal is increased too and vice versa as shown in Figure 4. The exegesis of this result is also relying on the active sites in the IRH. When the height of adsorbent media was small, the amount of media was less too; so the surface area and subsequently the number of active sites were less.

Therefore the amount of nitrogen molecules in SSAS that can be adsorbed on the surface of IRH media was low, comparing with greater adsorbent media height. Thus, the percentage removal of nitrogen from SSAS was decreased when the height of adsorbent media column was less. This result is in agreement with [12].

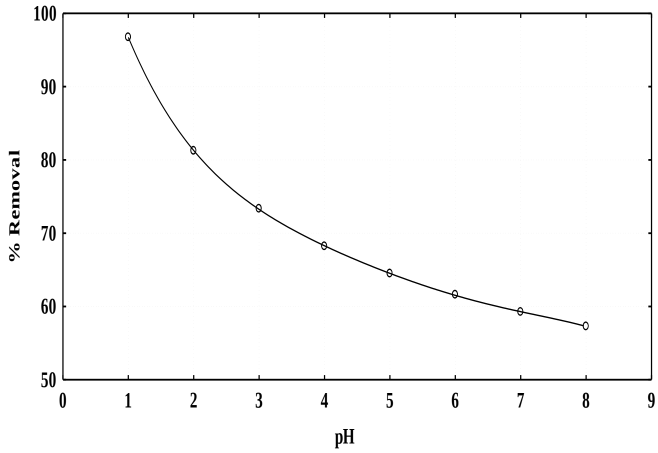

Figure 3. Effect of pH on the percent removal of nitrogen @ $C_{\circ}$= 1 mg/l, T_f=55°C, l = 0.4m, t=60 min. and F=5 ml/min

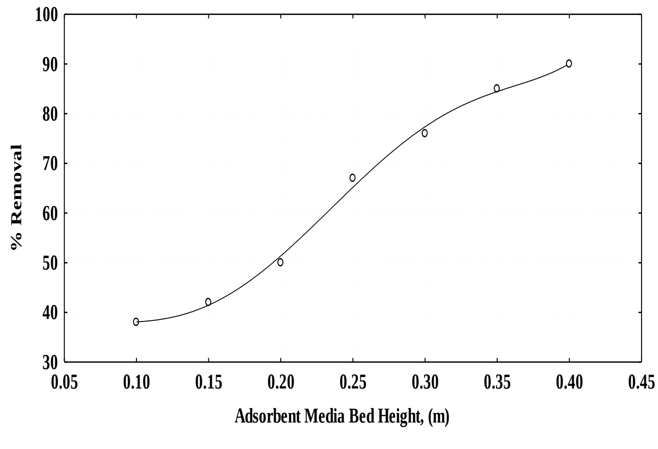

Figure 4. Effect of adsorbent media in packed bed column height (l) on the percent removal nitrogen @ $C_{\circ}$= 1 mg/l, pH=1, T_f=55°C, t=60 min. and F=5 ml/min.

3.4. SSAS Flow Rate Effect

To determine the effect of flow rate on the removal of nitrogen from SSAS, practical experiments were achieved after the fixation of other variables at their optimum values. The range of SSAS flow rate inlet to continuous fixed bed was varying between (5-100 ml/min). The final results pointed out that there is an inverse relation between flow rate and percentage removal, as shown in Figure 5. The maximum removal efficiency was 96.74% at F =5 ml/min. It is clear that the percentage removal of nitrogen was decreased with increasing SSAS flow rate and vice versa. When the SSAS flow rate is small, the solution may spend more time than when the solution enters at high velocity. So, the number of molecules that transfer from the solution to the adsorbent material IRH would be greater than that at high SSAS flow rate. Therefore, the percentage removal of nitrogen from SSAS was increased when the flow rate of SSAS was increased. This result is in agreement with [13].

3.5. SSAS Temperature Effect

The experiments of SSAS temperature effect on the percentage removal of nitrogen from SSAS using adsorption method with IRH were implemented at the range varying between (20-55°C) and all other variables are kept fixed at their optimum conditions. The results demonstrated that the nitrogen percentage removal was increased when the SSAS temperature increased too, i.e. there is a proportional relation (Figure 6). The maximum removal efficiency was 96.74% at T_f =55°C. When the feed temperature was changed, the removal process mechanism was also changing; because of the high temperature effect on the behavior of SSAS. Generally, any increase in the SSAS temperature will increase the movement of particles (ions or molecules) and lead to increase the speed of adsorption on the surface of adsorbent media. Furthermore, the pH of SSAS is also affected by the changing of feed temperature and decreased with increasing temperature; leading to increase the concentration of hydronium ions in the solution, i.e. increasing the positive charge on the surface of IRH and hence increasing The number of nitrogen molecules that are attracted on the active sites of adsorbent media .Therefore, the percentage removal of nitrogen is increased when the temperature of SSAS inlet to the adsorption unit is increasing too. This is in agreement with [14].

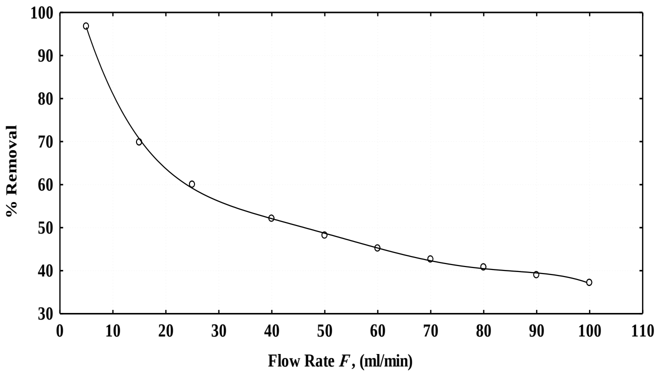

Figure 5: Effect of aqueous solution flow rate (F) on the percent removal of nitrogen @ $C_{\circ}$= 1 mg/l, pH=1, T_f =55°C, l= 0.4mand t=60 min.

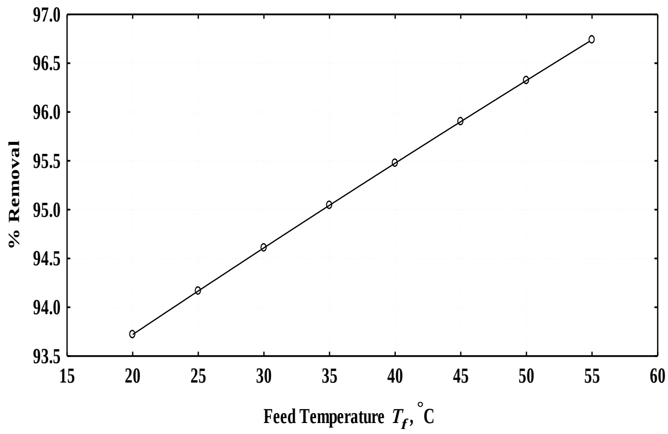

Figure 6: Effect of feed temperature (T_f) on the percent removal of nitrogen @ $C_\circ$= 1 mg/l, pH=1,l=0.4m, t=60 min. and F=5 ml/min.

3.6. Contact Time Effect

The effect of contact time on the adsorption process of nitrogen was studied in the range varied from (10-60 min) after all other operational conditions were fixed at their optimum values (Figure 7). The maximum removal efficiency was 96.74% at t =60 min. The results showed that there is a direct relation between the percentage removal and the contact time ; because the percentage removal of nitrogen is increasing with longer contact time. This may be due to that at long time and under a fixed flow rate (or velocity) of SSAS, the SSAS preordained further period in contact with the adsorbent media and the chance of molecules to transfer from the SSAS to the IRH surface was greater than that at short time. Thus at long time more molecules can be adsorbed by the media and the percentage removal of nitrogen from SSAS is increased with increasing contact time. This result is in agreement with [8].

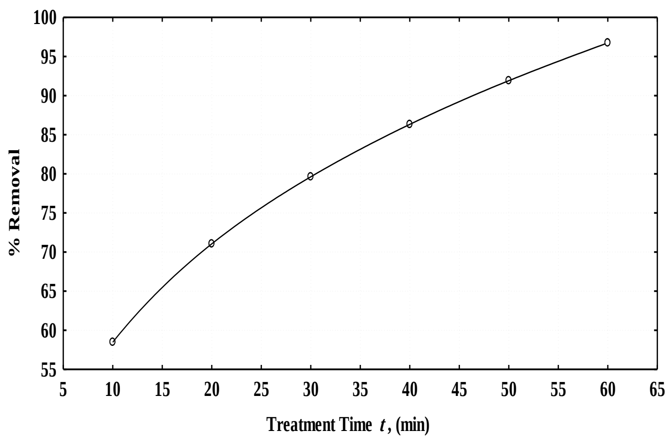

Figure 7: Effect of treatment time (t) on the percent removal of nitrogen @ $C_\circ$= 1 mg/l, T_f =55°C, pH=1, l=50cm, and F=5 ml/min

4. Statistical Model

A statistical model was performed on the results of practical experiments acquired from this investigation. Regression Analysis and π theorem were depended to find a mathematical equation between the nitrogen percentage removal and the SSAS feed temperature, SSAS flow rate, ambient pressure, solution pH, initial concentration of nitrogen, height of adsorbent media, i.e. IRH column, contact time and diameter of adsorption column. These parameters are related together as in equation (1) below, with a correlation coefficient (R^2) of 0.973.

$$\%R = 9.4882 \times 10^{-7} \left(\frac{T_f \,.\, P \,.\, l \,.\, C_{P_{sol}} \,.\, t}{F \,.\, d \,.\, C_{\circ} \,.\, g} \right)^{0.281} \left(\frac{1}{pH}\right)^{0.252} \qquad (1)$$

where:

$\%R$	Percent Removal of Nitrogenfrom SSAS
T_f	SSAS Feed Temperature, (K)
P	Pressure, (Pa)
l	Adsorbent Material Bed Height, (m)
$C_{P_{sol}}$	Heat Capacity of Aqueous Solution, (J/g. K)
F	SSAS Flow Rate, (m^3/s)
d	Internal Diameter of Adsorption Column, (m)
$C_{\circ}$	Initial Concentration of Nitrogen, (g/m^3)
t	Contact Time, (s)
g	Acceleration of Gravity, (m/s^2)

5. Utilization from Rice Husk after use

Utilization from the IRH after uses can be conducted by exploitation from it as a compost for tomato crop as follows: IRH waste, which has adsorbed the nitrogen from SSAS at different operating conditions, were segregated and classified according to their nitrogen content and utilization from these remaining samples as a raw material in synthesis of a fertilizer for tomato crop. A simple pots experiment was conducted using different ratios of nitrogen to IRH.

The ratios were between (0.01 to 0.1 wt. %) for nitrogen. IRH lingered with different ratios was firstly crashed to make a powder and mixed with the soil that is used for tomato crop production. Tomato crop results show bloomed and gave higher yield (18.25 wt. %) than tomato planted in the ordinary soil (Figure 8). It is known that rich-nitrogen organic fertilizers can increase yields of crops, vegetables and fruits, produce superior turf, healthy and deep roots, enhance uptake of fertilizers, creates vegetation in saline and poor soils, and promote ecological balance.

It can do that by enhancing soil structure and fertility through the addition of vital organic matter in the soil, by efficient transfer of fertilizer nutrients and micronutrients; because of the high chelation and cation exchange proportion of the active nitrogen component, increasing moisture holding capacity of soil, increasing microbial activity in the soil and enhancing plant cell biomass. Nitrogen affects soil and plant growth in different direct and indirect ways; it can affect physically through increasing soil water holding capacity, increases aeration of soils, improves soil workability, helps in resisting drought, improves seed bed, makes soil more friable or crumbly, reduces soil erosion and it can effect chemically by chelating nutrients for uptake by plants, possesses high ion-exchange capacity, increases buffering properties of soils, and increases percentage of total nitrogen in soils. Nitrogen can affect biologically through accelerating plant cell division and promoting growth, increasing germination of seeds and viability, increasing root respiration and formation, stimulating growth and proliferation of soil microorganisms, and adding in photosynthesis [6,8].

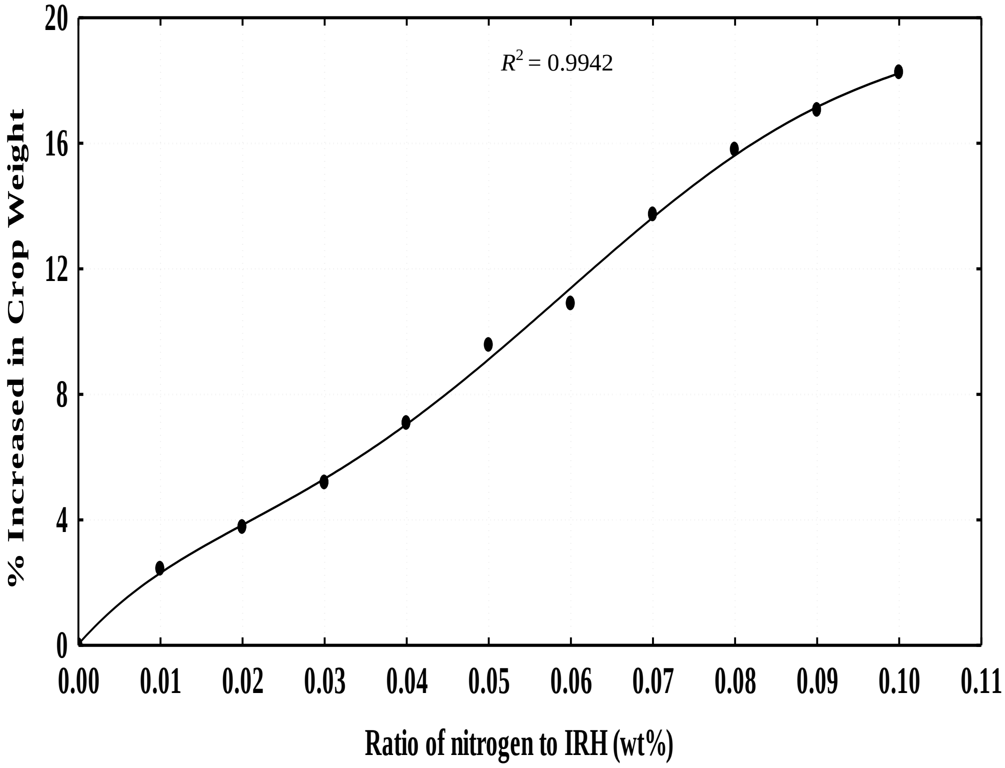

Figure 8.Percentage Increase in Tomato Crop Weight due to using the Prepared Compost, with R^2 = 0.9942

6. Conclusions

The following conclusions can be drawn:

- IRH showed a good ability to remove nitrogen from SSAS by using a fixed bed adsorption unit. So, this method could be recommended for the removal of nitrogen from wastewater in Iraq instead of other material; because it is available, low cost, economical, easy and simple to use, has a high ability to adsorb nitrogen, can be used several times by uncostly regeneration method and can be reused after treatment in other beneficial uses.
- The maximum removal of nitrogen was 96.74% at initial nitrogen concentration of 1 mg/l.

- The percentage removal of nitrogen was increased with decreasing flow rate of SSAS, pH and initial concentration of nitrogen, while was increasing with increasing of treatment time and the height of IRH adsorbent material.
- Good organic fertilizer can be prepared from the residual samples of IRH that had adsorbed the nitrogen from SSAS. So, the polluted waste (used IRH) was reused in an economic and eco-friendly method.

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