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EVALUATE THE POTENTIAL OF MICRO-ALGAE SPIRULINA IN NITRATE REMOVAL FROM URBAN WASTEWATER

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ABSTRACT

Large amounts of wastewater is produced in all societies that is hazardous to human health and the environment that should be treated before being discharged to rivers, lakes and ground. If the secondary treatment of sewage, agricultural, industrial and done, they waste large amounts of nitrogen and phosphorus [1].

In this paper, effects and use of bioreactors containing spirulina algae bioreactor were investigated for the removal of nitrate from sewage and influencing factors. Physical factors such as light, temperature, pH, stirring aeration and chemical agents are among microalgae culture, including significant factors influencing the growth of microalgae. Snake shape photo-bio-reactors form of three conventional reactors and medium Zarrouk were measured as appropriate culture medium was used to remove nitrates from municipal sewage. Microalgae for free algae and algae established in culture with different values of aeration (Lit / min zero and 3/1) to 3 liters of sewage in photo-bio-reactor, added and absorbed nitrate concentrations at different times by spectrophotometer (HACH DR/4000). The results showed that algae entrenched in the culture medium with aeration Debi 1/3 Lit / min has the highest efficiency about 80%. In addition, data nitrate equilibrium model Langmuir, Freundlich, De binin- Radushkevich and Temkin and to support pseudo-first model and the second model found that the isotherm of Freundlich and Temkin adsorption isotherms of the Langmuir and De binin- Radushkevich is more suitable to predict nitrate uptake by algae Spirulina. The pseudo-quadratic model provides a more accurate prediction.

Keywords: wastewater treatment, spirulina, microalgae, nitrates, sewage, photo bio-reactor

INTRODUCTION

Generally, wastewater treatment methods can be divided into three main categories: physical, chemical and biological. Rarely happens that one of the said methods can meet all the demands of the filtration system. So in most cases it is necessary to use a combination of the above methods. Purification plants work on the principle of one or a combination of methods employed is designed to perform specific operations. Rubbish removal, sedimentation and flotation are used, including physical methods to reduce pollution from sewage waste water treatment. Chemical methods of coagulants and other chemicals are used to remove specific compounds from wastewater and reduce the amount of pollution and suspended solids. In biological methods, microorganisms play a major role in the treatment process. Microorganisms such as bacteria (aerobic, anaerobic), fungi, algae, microbial biomass and vegetable, with its internal mechanisms, and absorb organic matter are used in wastewater to produce new cells and energy. Biological methods are able to lower costs, and to refine a wide range of pollutants. Methods of using extended aeration activated sludge process and biological wastewater treatment is IFAS including conventional processes. IFAS systems have greater benefits than conventional activated sludge processes (systems with suspended growth). These systems are in addition to the high resistance to organic loading and hydraulic shocks have the flexibility and power to further treatment.

Zamani et al. (2010) examined the consolidation and effects microalgae chlamydomonas for orthophosphate removal from urban wastewater. Stabilizing and increasing aeration affects the interaction between microalgae and bacteria, eliminates the amount of orthophosphate Tasyrgzashth [2] Mosta'jeran and coleagues (2005) examined the effect of green algae and blue-green pollutant load to reduce industrial wastewater using stabilization ponds. In this study, three algae were used including anabaena and oscillatoria and spirogyra and waste vegetable oil, sugar and slaughter [3].

Arash Javanshir et al. (2007) used Andontia signea oyster to remove nitrate and phosphate wastewater. The results showed that the number of algae in open systems, a significant amount of soluble phosphate and nitrate decreased by the algae in order to meet the critical needs. The results showed that the average performance in the compilation of mussels and algae on the uptake of nitrate and phosphate were 75/3, 76/3 percent, respectively [4].

Fierro et al. (2007) examined the removal nitrate and orthophosphate nitrogen released by microalgae Scenedesmus stabilization. Immobilized cells removed 70 and 94% of the nitrate and orthophosphate within 12 hours from the environment, while 20 percent nitrogen and 30 percent orthophosphate released cells were removed within 36 hours [5].

Klaus et al. (2014) studied the use of biological and physical-chemical methods for the removal of nitrate from contaminated groundwater. In this study, a combination of ion exchange and advanced biophysical treatment rotate was used as well denitrification reactor was exposed to ozone exposure successive ozone [6].

On the other hand, in study by Zhang (2014) 4 activated sludge foam base with PCL (PCL) were used to remove nitrogen. The results showed that the molecular weight loss, increased nitrogen biodegradability. Also, PCL with a higher average molecular weight showed nitrate removal than other carriers PCL. [7].

Yi et al. (2014) reported that bio-electrochemical reduction is a safe method for the removal of nitrate compounds. They used an ion exchange membrane reactor. However, this method has many problems, because bacteria other cathodic toxic components in the waste water [8].

Maria T.P. et al. used 4 types of brown algae as ski, flume, Spiranthes and Hilerporiya disguised as normal for the removal of heavy metal cations in petrochemical wastewater. It also showed that Hilerporiya has a greater absorption capacity than other algae and the balance of the Langmuir adsorption model [9].

Spirulina was recognized internationally in 1963. Algae growth requires the trace elements (Zn, Si, Mn, Fe, Co, Cu, Mo) elements most pressing (C, N, P, S, K, Mg, Ca). Thus, resulting in the growth and metabolism absorb heavy metals and nutrients as their ability and disappeared after a period of absorption and sludge (biomass) from the result that the elements of food high and good quality and can be used as livestock feed. Therefore algae, especially spirulina has a good potential for urban wastewater treatment. Therefore, the present study investigated the factors affecting the performance of the algae and is trying to be modeled uptake kinetics nitrite.

MATERIALS AND METHODS

Material

Waste characteristics

Physical and chemical properties of 4 were synthesized wastewater samples are shown in Table 1 for testing. Indicators of pollution include: total solids, total dissolved solids (TDS), sustainable materials, volatile compounds, total suspended solids (TSS), BOD5, total nitrogen (as N), total phosphorus (as P), chloride, alkalinity (as CaCO3), oils and fats.

Environmental specifications algae growth

In this article Zarrouk medium was used that is suitable for the cultivation of spirulina algae cc200. Medium characteristics are shown in Table 2.

Table 1: The physical and chemical properties of synthetic sewage

4 Sewage synthesized	3 Sewage synthesized	2 Sewage synthesized	1 Wastewater	Sewer components
350	350	350	1050	**Total solids**
250	250	250	820	**Total dissolved solids, TDS**
145	145	145	510	**Sustainable materials**
105	105	105	312	**Volatile substances**
100	100	100	310	**Total suspended solids, TSS**
133	133	133	260	**BOD_5**
575	575	575	575	**Total nitrogen (N)**
0	0	0	20	**Total phosphorus (in P)**
0	0	0	150	**Chlorides**
0	0	0	204	**Alkalinity (as CaCO3)**
0	0	0	130	**Oils and lipids**

Table 2: Components medium Zarrouk

The quantities needed	Names of parts medium
4gr	$NaHCO_3$
2/5gr	$NaNO_3$
0/04gr	$CaCL_2$
0/8gr	EDTA
1gr	NaCL
1gr	K_2SO_4
1gr	$Fe_2(SO_4)_3$
0/5gr	Na_2HPO_4
1gr	$ZnSO_4$
0/2gr	$MgSO_4$
۱ cc	Trance Elements

Algae grow between 25 and 37 ° C ambient temperature and 40 watts fluorescent held for 24 hours over the growth tank. The pH was maintained between 8 and 9.

Snake-shaped photo-bioreactor

Snake-shaped bioreactor is systems in which several transparent tube, with direct and specific order by the U-shaped tubes are connected to the number of loops to create a smooth horizontal or vertical. Transactions gas and food additives are done in the two tubes separately.

Medium rotation is performed between the light and the photo-bioreactor gas exchanger by a pump or an air lift section. Temperature control is an important issue in these systems. The optimum temperature for growth of the microalgae that is higher using this system, and severe agitation and intermittent exposure can be achieved higher growth rates.

Methods

Test Method

The study of snake-shaped photo bio-reactor was used to remove nitrates from municipal sewage. This photo bio-reactor was made in the batch position and the 20-liter gallons of mineral water. 3 other containers with a capacity of 15 liters were used simultaneously.

To evaluate the effect of aeration on the performance of microalgae, aerated and non-aerated at 4 Lit / min 3/1 were used for different treatments.

- Treatment Fr: 100 g microalgae established without aeration in addition to 3 liters of sewage
- Treatment Fr 1/3: 100 g microalgae stabilized with 3 liters of wastewater aeration plus synthesized
- Treatment Im: 100 g free microalgae plus 3 liters of synthetic wastewater without aeration
- Treatment Im 1/3: 100 grams of fine free algae plus 3 liters of wastewater aeration synthesized with the preparation, lit 3 of the treatmets were cast in photo-bioreactor to the growth of algae, nitrate removal in a 30-day period investigated. Samples were taken at different time period and the amount of nitrate samples was determined by spectrophotometer (DR / 4000 (HACH)).

Adsorption

Adsorption is the interaction between atoms or molecules adsorb onto a solid surface material that is divided into two categories: physical adsorption and chemical adsorption. To determine the nature of the absorption can be two factors help to adsorb and absorb temperature. Chemical absorption, physical adsorption occurs at temperatures far above and by changing the solid level. Tests show that the amount of absorption depends on an absorbing function of the concentration of soluble characteristics, temperature, nature and surface area of adsorbent e. Often the amount of absorption is called as a function of concentration at a constant temperature to obtain the adsorption isotherm.

Langmuir isotherm

Langmuir monolayer adsorption isotherm used to absorb the same absorption levels with a limited number of positions, and it is one of the laws of non-living biomass and is true in many cases.

Langmuir adsorption equation2-1 is as follows.

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \quad (1\text{-}2)$$

In equation 1.2, q_e is the amount of contaminants absorbed per unit mass of biomass (mg / g) or (mmol / g) at equilibrium, balance and C_e represents the equilibrium concentration of pollutants and b shows the absorbent and adsorbent affinity.

Freundlich isotherm

Equation 2-2 shows Freundlich isotherm absorption, which represents the relationship between the absorption layer and the surface is heterogeneous adsorbent analysis.

$$q_e = K_f C_e^{\frac{1}{n}} \quad (2\text{-}2)$$

2-2 and n are constants in the Freundlich model which represents the absorption capacity and absorption rate are respectively the slope and width of the linear equation derived from the source form.

Depinin – Radushkevich Isotherm

Depinin – Radushkevich Isotherm was used to determine the nature of the brief adsorption. It is non-linear equation to equation 2-3.

$$\ln q_e = \ln q_{\max} - \beta \varepsilon^2 \quad (3\text{-}2)$$

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \quad (4\text{-}2)$$

In equation 3-2, β shows the adsorption coefficient average energy-related activity, ε is the potential that is shown in 4-2 equation, q_e is the amount of nitrate nitrogen in the absorbent (mg / Lit) and $q_{\max}$ is single-layer capacity (mg / Lit).

Temkin Isotherm

Isotherm equation includes a factor that states the speed the interaction between the components of absorbing the heat of adsorption so that all the molecules in the lining are linearly reduced. The reason is absorbing forces of repulsion and attraction, the same distribution of the connective maximum energy. In addition, it is assumed that reduce heat absorption compared to the log state is linear. Equation 5-2 shows the relationship between Temkin isotherms.

$$q_e = B_T Ln(A_T) + B_T \quad (5\text{-}2)$$

Equation 5.2, T represents the absolute temperature in Kelvin, R is gas constant, B_T is constant and A_T is fixed to the heat absorption associated with maximized energy balance linked bonds, respectively.

Uptake kinetics

While, different kinetic models has been used such as model-like first and second grade to compare the accuracy of data capture with catchy biological nitrate. Adsorption process of any mass transfer of both external and internal foreign is not considered. The adsorption kinetics can be deposited ion concentration in a solution of review. Adsorption capacities are controlled in solid solution, which includes the distribution process.

Pseudo-first grade equation

First order kinetic equation shown in equation 6-2, examines the nitrate ion adsorption on Spirulina microalgae using data behavior.

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t \qquad (6\text{-}2)$$

Equation 6-2, q_e is the concentrations of absorbing at equilibrium, q_t is the concentration of nitrate ions adsorbed at time t and k_1 is fixed rate equation first.

Pseudo quadratic equation

Pseudo-second kinetic equation is shown in equation 7-2. Equation 7-2 k_2 is the constant of the quadratic equation.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (7\text{-}2)$$

RESULTS AND DISCUSSION

The nitrate removal

In a 30-day period, spirulina algae were investigated for the removal of nitrate from municipal wastewater performance. Results are shown in Figure 3-1.

The data from Figure 3-1 shows that nitrate uptake was very low initially by Spirulina algae in bio-reactors for municipal waste water in different scenarios, and the amount increases with the passage of time and ensure compatibility with the algae. So that in the process of absorption, the absorption performance on the first day, which is nearly 20% increase Manddr time during the 30 days, the yield is 60%. Over time, in addition to algae, it becomes compatible with the environment, the population and its growth, and for treatments Fr, Fr 1/3 and Im from the eighteenth to the next day for treatment Im 1/3 of the twelfth day has been improved after algae activity to absorb nitrate.

Moreover, comparing the performance of systems in both aeration and rest state show that the Spirulina microalgae increases performance by increasing air flow, especially in the days when the contact time between the absorbing (nitrate) and absorbent (Spirulina microalgae) arrives to the end. As diagram 1-3 shows that in addition to the exposure time, the concentration of biomass in both aeration and living olays an active role in the absorption of the absorbing component. In other words, by increasing the concentration of the absorbent, the absorption of biological nitrogen increases. As shown in Figure 3-2, the nitrate uptake by Spirulina micro-algae in environments with low pH lowers than that in environments with a pH higher. So that the absorption efficiency of biological nitrogen pH = 7 level of 5 percent and pH = 9, Spirulina micro-algae can absorb 35% nitric acid.

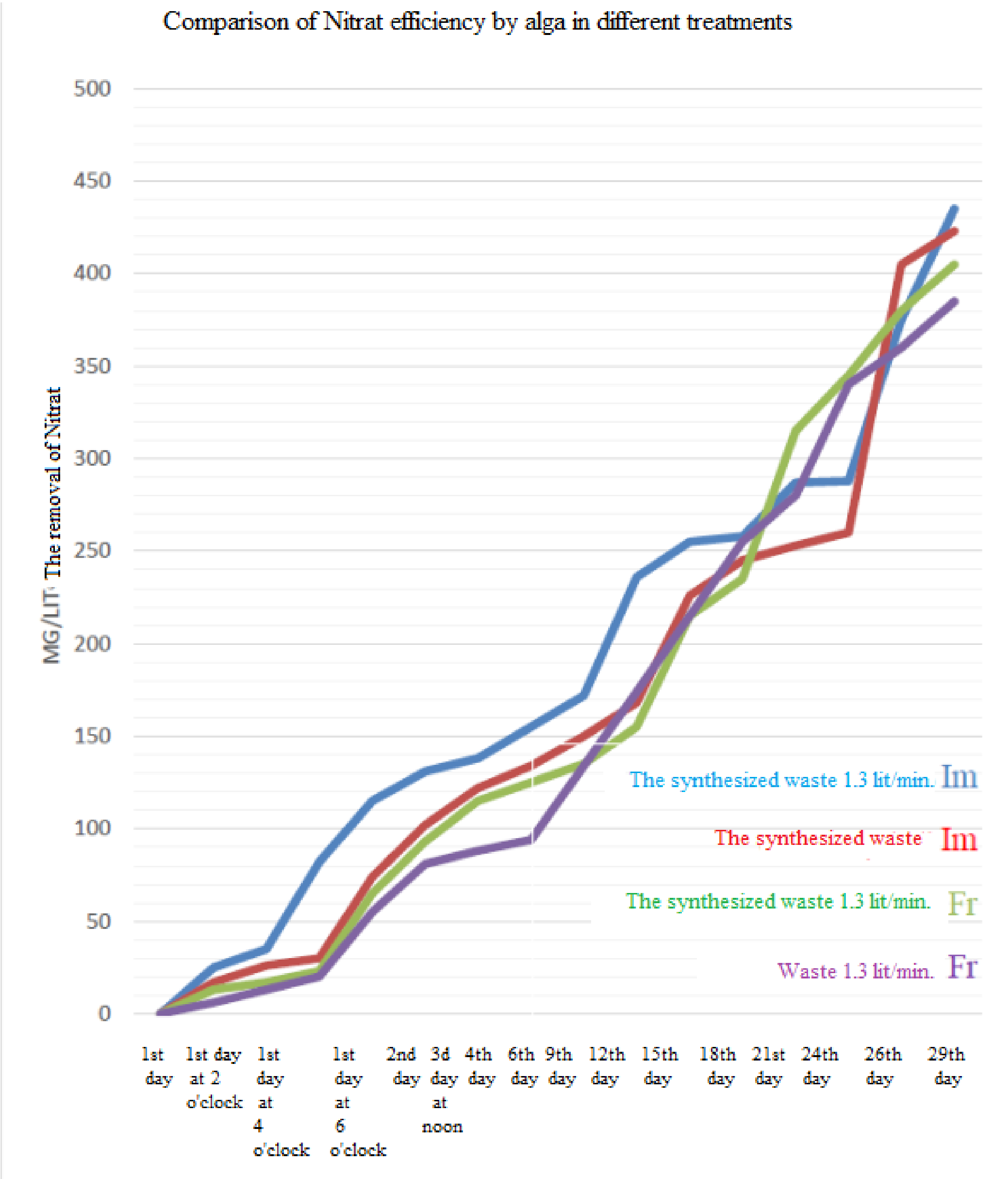


Fig. 1-3. Nitrate removal by the Spirulina microalgae bioreactor containing within 30 days

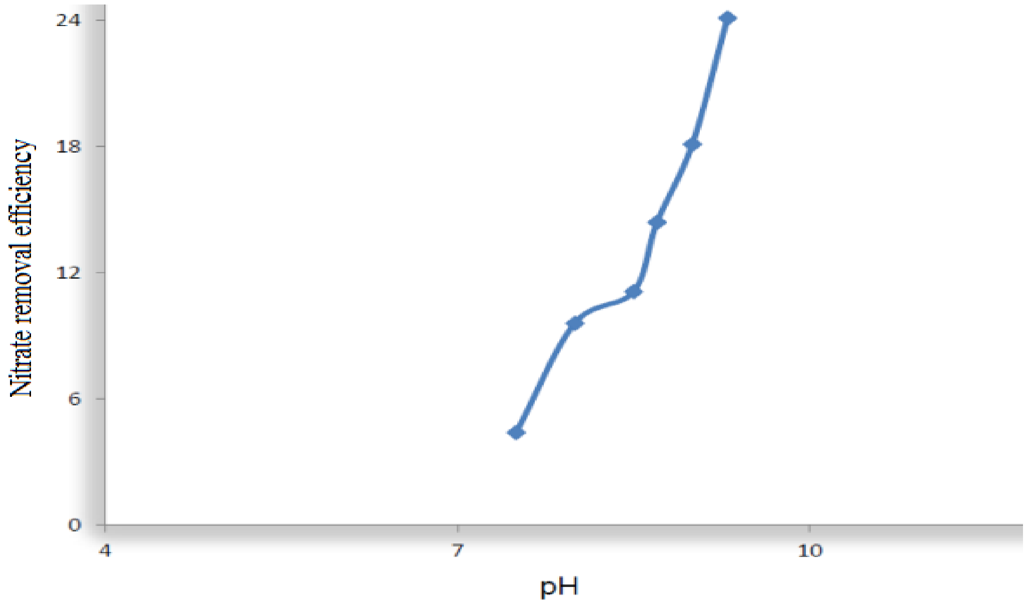


Fig. 2-3. Effect of pH on nitrate uptake efficiency in absorbing Spirulina micro-algae

As shown in Figure 3-3, the efficiency of absorption depends on the amount of adsorbent. The more absorbent in the solution, the number of absorbed sites increases and therefore the absorption efficiency increases. This is due to the small mass of adsorbent components and reduces the surface area of the effective sites adsorbent occur with interference and electrostatic interactions.

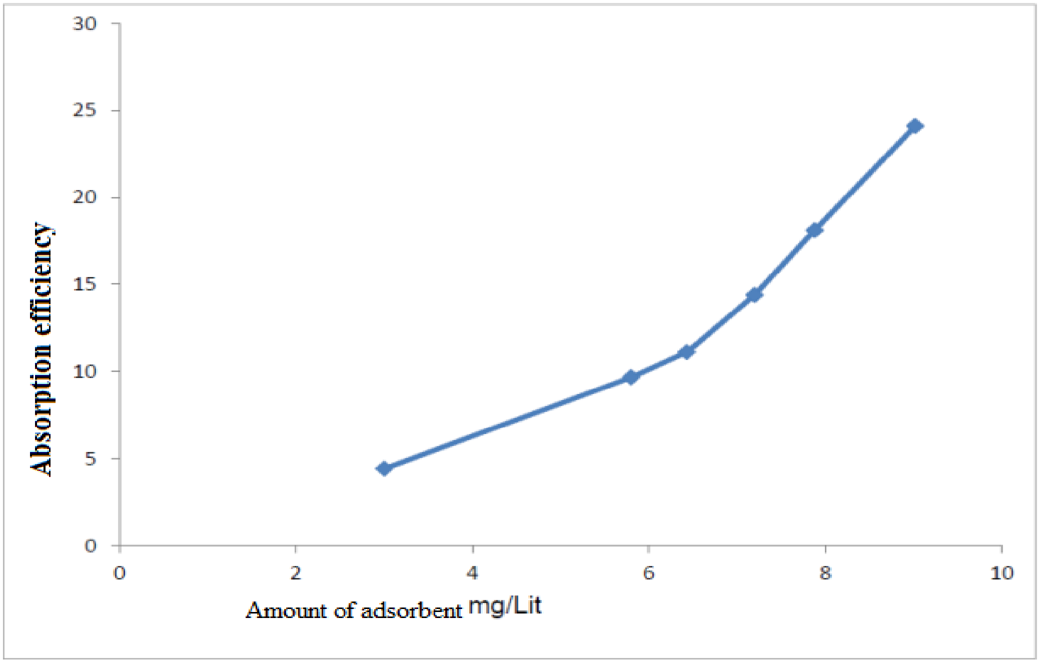


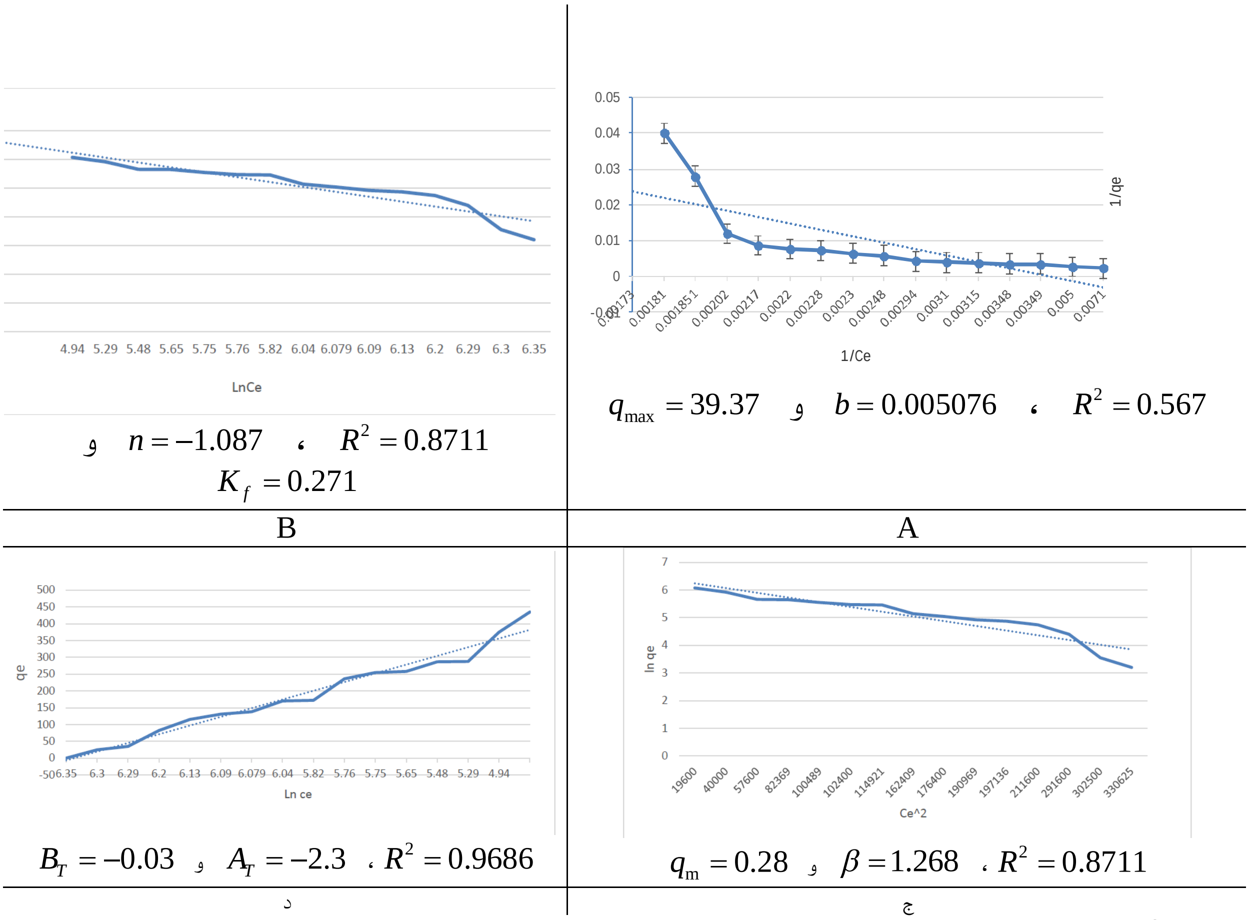
Fig. 3. 3. Absorbing effect of Spirulina microalgae nitrate uptake efficiency

The sorbent particle size reduction, absorption and time to balance increased due to an increase in the effective surface area of the adsorbent. If the particle size of the adsorbent must be a regeneration cycle withstand the operating pressure conditions. The absorbing particles should increase the mechanical strength of particles such as rising pelletizing.

Adsorption isotherms

In this paper, adsorption isotherms were studied at a constant temperature of 25 ° C to evaluate the performance of sorbent (biomass) at a constant temperature.

In Figure 3-4, different isotherms are shown such as Langmuir, Freundlich, Depinin-Radushkevich and compliance with correlation coefficients and constants.



B: و $n = -1.087$ ، $R^2 = 0.8711$ $K_f = 0.271$

A: $q_{\max} = 39.37$ و $b = 0.005076$ ، $R^2 = 0.567$

د: $B_T = -0.03$ و $A_T = -2.3$ ، $R^2 = 0.9686$

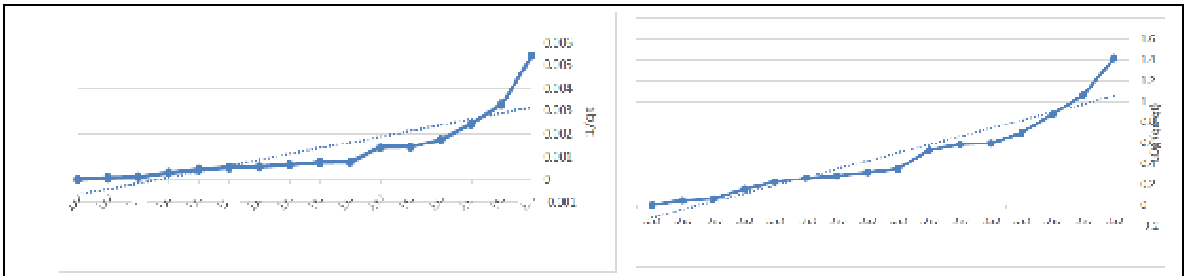
ج: $q_m = 0.28$ و $\beta = 1.268$ ، $R^2 = 0.8711$

Fig. 4-3. A. Langmuir isotherm, B. , Freundlich isotherm , c , Depinin - Radushkevich isotherms and isotherm deference for nitrate uptake by100 g / Lit Spirulina microalgae during 30 days

As determined according to the correlation coefficient can be concluded that compliance isotherm is excellent agreement with the data. Therefore, it can be stated that nitrate uptake has been laminated by micro-algae Spirulina. It should also be noted that the adsorption isotherms Langmuir, Freundlich and Depinin-Radushkevich are in good agreement with data.

Uptake kinetics

Figure 5-3 shows the kinetics of pseudo first and second grade for nitrate uptake by living biomass at a temperature of 25 ° C.



و $k_2 = -210.486$ ، $R^2 = 0.716$

$q_e = -1.11$

B

و $k_1 = -0.281$ ، $R^2 = 0.8932$

$q_t = -4.99$

A

Fig. 5-3. Nitrate uptake by micro-algae Spirulina compliance with a) pseudo-first equation and b) pseudo-quadratic equation

Although pseudo-first order is more linear, according to the kinetics of pseudo correlation coefficients can be said that the first and second degree of any of the nitrate uptake by micro-algae Spirulina is not linear.

CONCLUSION

The present study results showed that blue-green Spirulina algae is better adsorbent to remove nitrates from municipal waste because of its cost-effectiveness and efficiency in comparison with other elements such as heavy metals, nitrate uninstall. The results showed that with increasing contact time through aeration, pH, nitrate absorption efficiency increases. Compliance with different isotherms adsorption data showed that for the special process used, isothermal deference to the isotherms, sorption process provides a better prediction of the process. Correlation coefficient of experimental data consistent with the kinetics of pseudo-first and pseudo-second-order kinetic modeling showed that the performance of micro-algae Spirulina is not suitable in nitrate removal from urban wastewater.

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Abbreviations:

q_e: The amount of contaminants absorbed per unit mass of biomass (mg / g) or (mmol / g) at equilibrium.

C_e : Equilibrium concentration of pollutants is not absorbed or absorbed concentration in solution at equilibrium (mg / Lit).

b: Constant to show the affinity between the absorbent and adsorbent

K_f : Constant absorption represents Freundlich model

n: fixed Freundlich model represents the intensity of the absorption capacity of single-layer (mg / lit)

q_{max}: Factor activity related to energy adsorption medium. Potential absorption

T: absolute temperature in Kelvin scale.

R: universal constant of gases (8.314).

B_T: Fixed number of heat absorption.

A_T: Fixed links corresponding to the balance that is the binding energy maximized.

T: time

q_t: the concentration of nitrate ions adsorbed at time t (mg / g).

k_1 : Pseudo first order rate constant ($\min^{-1}$)

k_2 : Pseudo second order rate constant ($\min^{-1}$)