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Removal of Nickel Ions Using A Biosorbent Bed (*Laminaria saccharina*) Algae

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Abstract

The present study aims to remove nickel ions from solution of the simulated wastewater using (*Laminaria saccharina*) algae as a biosorbent material. Effects of experimental parameters such as temperature at (20 - 40) C^0, pH at (3 - 7) at time (10 - 120) min on the removal efficiency were studied.

Box-Wilson method was adopted to obtain a relationship between the above three experimental parameters and removal percentage of the nickel ions. The experimental data were fitted to second order polynomial model, and the optimum conditions for the removal process of nickel ions were obtained.

The highest removal percentage of nickel ions obtained was 98.8 %, at best operating conditions (Temperature 35 C^o, pH 5 and Time 10 min).

Keywords: Nickel Ions, Biosorbent Bed, (*Laminaria saccharina*) Algae

Introduction

Heavy metals are generally considered to be those whose density exceeds 5 g/cm^3 [1]. Removal of heavy metals from industrial wastewater is of primary importance because they are not only cause contamination of water bodies but also they are toxic to many life forms. Industrial processes generate wastewater containing heavy metal contaminants. Since most of heavy metals are non- degradable into nontoxic end products, their concentrations must be reduced to acceptable levels before discharging them into environment. Otherwise these could pose threats to public health and/or affect the aesthetic quality of potable water [2].

According to World Health Organization (WHO) the metals of most immediate concern are chromium, copper, zinc, iron, nickel, mercury and lead [3].

Nickel ions represent a serious environmental problem since they are widely used in many industries and general applications. Among them are: industrial effluents, industrial fertilizers, catalysts, gears, magnets, airbag valves, electronics, tooth protects, exhaust smokes, stainless steels, etc. [4].

Ni (II) is a known environmental pollutant and its removal is of major concern because nickel compounds are carcinogenic and also can cause asthma. Another common adverse health effect of Ni (II) is skin allergy [5].

The removal of heavy metal ions from aqueous solutions can be achieved by several processes, such as chemical precipitation, biosorption, adsorption, solvent extraction, reduction, coagulation, oxidation, reverse osmosis, flotation, ultra filtration and ion exchange [6, 7, 8].

The search for new technologies involving the removal of toxic metals from wastewaters has directed attention to biosorption, based on metal binding capacities of various biological materials. Biosorption can be defined as the ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated or physico-chemical pathways of uptake [9]. Algae, bacteria, fungi and yeasts have proved to be potential metal biosorbents [10]. The major advantages of biosorption over conventional treatment methods include [11]: low cost, high efficiency, minimization of chemical and /or biological sludge, no additional nutrient requirement, regeneration of biosorbent and possibility of metal recovery.

Algae biomass has proven to be highly effective as well as reliable and predictable in the removal of heavy metals from aqueous solution. The term algae refer to a large and diverse assemblage of organisms that contain chlorophyll and carry out oxygenic photosynthesis [12]. There are seven divisions of algae: four of which contain algae as members. Divisions which include the large visible algae are: cyanophyta (blue-green algae), Clorophyta (green algae), Rhodophyta (red algae), and Phaeophyta (brown algae). These divisions are subdivided into orders, which are subsequently divided in to families and then into genus and species [13].

Sargassum sp. algae was reported to be able to absorb one or more heavy metal ions, including: K, Mg, Ca, Fe, Sr, Co, Cu, Mn, Ni, Zn, As, Cd, Mo, Pb, Se, Al ions with good metal uptake capacity [14, 15].

Laminaria saccharina is a type of brown algae, which is in the form of long grass (0.5 - 14.0) m and that the dominant form in this type of algae is the form spore. This type of algae is present on the beaches, marine tidal low and at depths of up to 30 m in the shores of the Atlantic and Pacific and the Mediterranean Sea [16].

The aim of the present work is to investigate the efficiency of *Laminaria saccharina* algae as biosorbent material to remove nickel ions from solution of simulated wastewater. The effects of temperature, pH, and time on the removal efficiency were studied.

Experiments and Material

Biosorbent Material and Chemicals

A *Laminaria saccharina* algae were used as biosorbent material for the removal of nickel ions. The algae were collected from AL-Lattakia from Syria in July of 2010. 2000 gm of algae were washed and dried at 105 ^oC for 24 hrs, then grinded and sieved to obtain 0.75 mm diameter of a biosorbent particales.

Nickel sulfate hexahydrate $NiSO_4.6H_2O$, M.wt= 262.8486 gm/mol. (Ferak, Germany) used to prepare a solution of the simulated wastewater contains 10 mg/L of nickel ion (Ni^{+2}). Hydrochloric acid [1M] and Sodium hydroxide pellets were used to adjust pH to the desired value.

Equipment

- Atomic Absorption Spectrometer: AAS (Norwalk, Connecticut, U.S.A) used to measure concentrations of soluble nickel.
- pH-Meter: the pH of the solution was measured by pH bench meter (I H250, Bench model, USA).
- Digital electrical balance (Sartorius, 1500 gm capacity and 0. 1 gm

- accuracy) used for weighting the materials used in this work.
- Several types of sieves were used to obtain 0.75 mm diameter of a biosorbent particales.
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Preparation of Simulated Solution

Generally, to achieve a concentration of 1000 mg/L of simulated wastewater, a mass of heavy metal salt was added to distilled water by assuming complete dissolution and calculated as follows [17]:

$$W = V \times C_i \times \frac{M.wt}{At.wt} \qquad \ldots(1)$$

Where:

W: Weight of heavy metal salt (mg).

V: Volume of solution (1L).

C_i: Initial concentration of metal ions in solution (mg).

M.wt: Molecular weight of metal salt (g/mole)

At.wt: Atomic weight of metal ion (g/mole)

Nickel was added in the form of nickel sulfate hexahydrate ($NiSO_4.6H_2O$). Nickel (Ni^{+2}) has a molecular weight of (58.69) g/mole. To determine the amount of $NiSO_4.6H_2O$ necessary to prepare a solution of the simulated wastewater contains (10) mg/L of nickel ions (Ni^{+2}), the following equation is used:

$$NiSO_4.5H_2O\ (s) \longrightarrow Ni^{+2}\ (aq) + SO_4^{-2}\ (aq) + 5H_2O\ (l) \qquad \ldots(2)$$

$$W = 1(L) \times 10\ (mg) \times \frac{262.8486\ (g/mole)}{58.69\ (g/mole)}$$

W= 44.8 mg $NiSO_4.5H_2O$

A Biosorption Unit

Schematic diagram of the biosorption unit is shown in Fig. (1) which consist of the following parts:

- Tank: 250 L volume to store the solution of simulated wastewater consists 10 mg/L of nickel ions (Ni^{+2}).
- Pump, power consumption 1.5 kW / (220 – 240 V) from (Haake W19), to pumping the simulated solution at constant volumetric flow rate 1.5 cm^3 /sec.
- Glass column: 100 cm height, 5 cm diameter and 2.5 mm wall thickness. Two circular glass discs 5 cm thickness were installed at a distance of 20 cm from the upper and lower end of the glass column. The discs were perforated by 0.5 mm holes maintain a uniform dawn flow of simulated solution.
- A biosorbent bed: (50 cm height and 5 cm diameter) were made by put (500) gm of dry particle of biosorbent material (0.75 mm particle diameter of *Laminaria saccharina*) between two circular glass discs above.

Moisture and ash contents of the biosorbent material but also the porosity and bulk density of the bed were determined in accordance of a reference method [17]. Some properties of biosorbent material and bed are shows in table (1).

Table 1, some properties of biosorbent material and bed

No.	properties	Value
1-	Moisture	9%
2-	ash contents	0.5%
3-	porosity	0.49
4-	Bulk density	0.5 gm./cm^3

Biosorption Process

A solution of simulated wastewater in the stored tank was pumped at constant volumetric flow rate 1.5 cm^3 /sec at the top of the column above at temperature (20-40) ^oC, pH of (3-7) and time (10-120) min. Samples of treated water 100 ml were taken from the bottom of column, these samples were filtered and the residual concentration of nickel ions was determined by ASS.

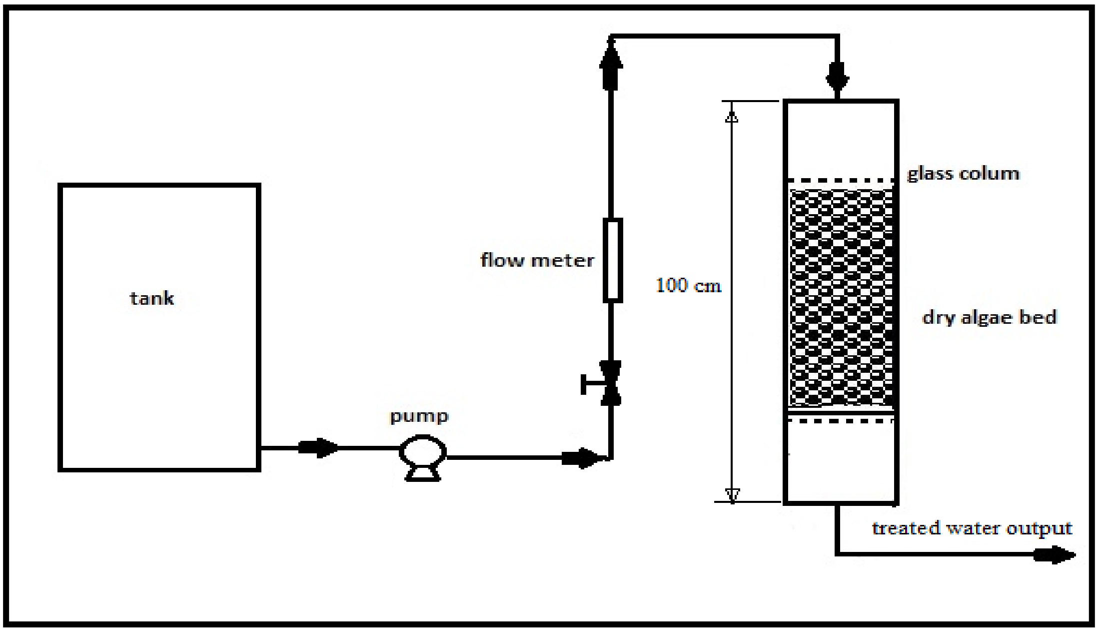

Fig. 1, Schematic Diagram of the Biosorption Unit

Results and Discussion

Analysis and optimization of Experimental Results:

The response of experimental work conducted according to Box-Wilson [18], is represented by the removal percentage of nickel ions (**R%**):

$$R\% = (C_o - C_f) / C_o \times 100\% \quad \ldots(3)$$

Where:

C_o: Initial concentration of nickel ions (mg/L).

C_f: Final concentration of nickel ions (mg/L).

It is fitted by a second–order polynomial mathematical model. A second order polynomial equation is employed in the range of the independent three variables (**X_1**= Temperature, **X_2**= pH and **X_3 =** Time) were considered. The general form of a second order polynomial can be represented in the following equation:

$$R\%=B_0+B_1X_1+B_2X_2+B_3X_3+B_4X^2 +B_5X^2{}_2+B_6X^2{}_3+B_7X_1X_2 + B_8X_1X_3 + B_9X_2X_3 \quad \ldots(4)$$

Using the real data of central composite design is given in table (2) to determine the coefficients of equation (4) by using STATISTICA software ver. 6. Equation (4) can be written as follows:

$$R\%=0.45+2.5886X_1+18.995X_2+ 0.32276X_3 -0.0556X_1^2-2.5064X_2^2- 0.0006X_3^2+0.2833X_1X_2-0.0142X_1X_3 - 0.0882X_2X_3 \quad \ldots(5)$$

Correlation coefficient (R) =0.9684

Statistical analysis was made by using the above software according (T-test) and least significant differences (L.S.D) at P-Value equal or less than (0.05). Table (3) shows that all coefficients of equation (4) were significant.

He optimization procedure was applied to equation (5) to find the optimum operating conditions (temperature, pH and time) by:

a. Differentiating equation (5) for three times once; with respect to X_1, X_2 and X_3.
b. Setting the resulting equations to zero.

c. Solving these equations simultaneously to find the optimum values of variables (X_1, X_2 and X_3).
d. Conducting a second differentiation to test for the sufficient conditions to ascertain that the optimum point is indeed a maximum point.

The results of optimization indicate that the optimum conditions are:

$X_1 = 35\ ^oC$; $X_2 = 5$; $X_3 = 10$ min

The removal percentage of nickel ions was equal to 98.8%.

Table 2, Coded and Real variables and removal percentage of nickel ions using central composite routable method

Exp. No.	Coded variables			Real variables			(R)%
	X_1	X_2	X_3	X_1	X_2	X_3	
1	1	1	1	35.7	6.154	96.75	30.287
2	-1	1	1	24.2	6.154	96.75	33.837
3	1	-1	1	35.7	3.845	96.75	41.209
4	1	1	-1	35.7	6.154	33.24	80.698
5	-1	-1	1	24.2	3.845	96.75	52.632
6	-1	1	-1	24.2	6.154	33.24	74.243
7	1	-1	-1	35.7	3.845	33.24	79.054
8	-1	-1	-1	24.2	3.845	33.24	80.742
9	1.732	0	0	40	5	65	56.750
10	0	1.732	0	30	7	65	49.697
11	0	0	1.732	30	5	120	29.124
12	-1.732	0	0	20	5	65	63.085
13	0	-1.732	0	30	3	65	61.196
14	0	0	-1.732	30	5	10	98.288
15	0	0	0	30	5	65	65.037
16	0	0	0	30	5	65	65.037
17	0	0	0	30	5	65	65.037
18	0	0	0	30	5	65	65.037

Table 3, Statistical analysis according (T-test) and least significant differences (L.S.D)

Variables	**Coef.**	**SE**	**T-test**	**P-value**
Constant	0.45	12.60	0.04	0.973
$\mathbf{X_1}$	2.5886	0.5247	4.93	0.001
$\mathbf{X_2}$	18.995	2.451	7.75	0.000
$\mathbf{X_3}$	0.32276	0.07688	4.20	0.003
$\mathbf{X_1^2}$	-0.055574	0.007461	-7.45	0.000
$\mathbf{X_2^2}$	-2.5064	0.1863	-13.45	0.000
$\mathbf{X_3^2}$	-0.0005838	0.0002464	-2.37	0.045
$\mathbf{X_1\ X_2}$	0.28325	0.04903	5.78	0.000
$\mathbf{X_1\ X_3}$	-0.014209	0.001783	-7.97	0.000
$\mathbf{X_2\ X_3}$	-0.088180	0.008878	-9.93	0.000
Significance equal or lower than (0.05). ($P \leq 0.05$)				

Effect of Operating Variables on Biosorption

Effect of Temperature

The variation of removal percentage of nickel ions with temperature of simulated wastewater is shown in Fig. (2). It can de concluded that maximum removal percentage of nickel ions has been obtained at (35) ^{o} C.

This suggests that biossorption between algal biomass and metal could involve a combination of chemical interaction and physical adsorption. With increasing temperature above (20 to 35) ^{o} C, pore in the algae enlarge resulting in an increase of the surface area available for the sorption, diffusion, and penetration of nickel ions within the pores of algae causing an increase in sorption [19]. Also increasing temperature is known to increase the diffusion rate of adsorbate molecules within pores as a result of decreasing solution viscosity and will also modify the equilibrium capacity of the adsorbent for a particular adsorbate.

Further increase in temperature (above 35 ^{o}C) leads to decrease in the removal percentage. This decrease in biosorption efficiency may be attributed to many reasons: increasing in the relative escaping tendency of the heavy metal from solid phase to the bulk phase, deactivating the biosorbent surface, or destructing some active sites on the biosorbent surface due to bond ruptures [20] or due to the weakness of biosorption forces between the active sites of the sorbents and sorbate species and also between the adjacent molecules of sorbet phase [21].

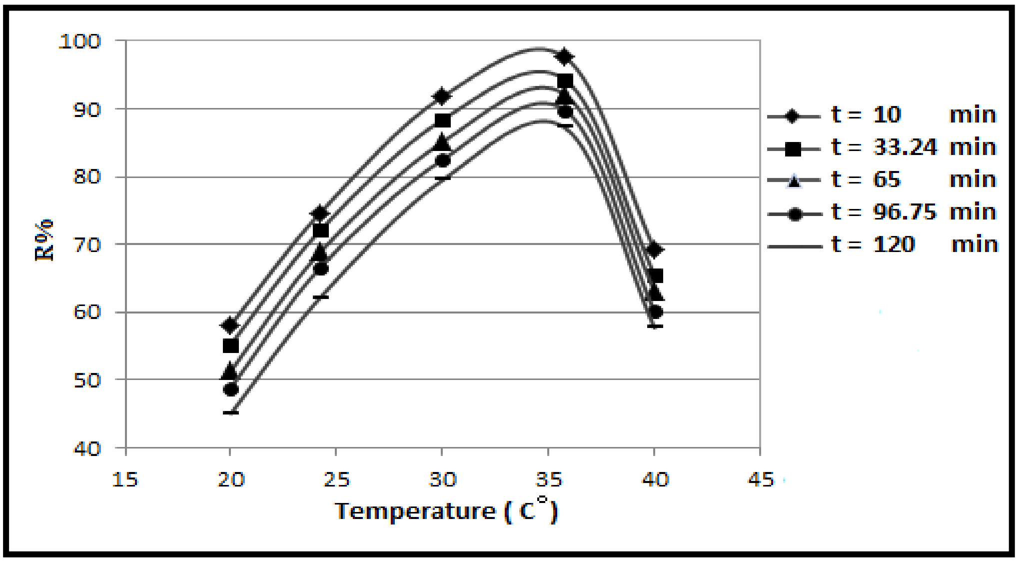

Fig. 2, Effect of temperature on the removal percentage of nickel ion at different times

Effect of pH

In order to examine the effects of pH on removal efficiency of the nickel ions, several experiments were carried out at various initial values (from 3 to 7) with different times (from 10 to 120 min). The experimental data showed that the optimum pH for removal percentage of nickel ions was (5); this is in good agreement with previous studies [22, 23]. At pH below (3), the positive charge (H^+) density on the sites of biomass surface minimizes metal sorption, and above (5), metal precipitation is favored. Fig. (3) Shows the effect of pH on the biosorption efficiency of nickel ions at different times.

Effect of Time

The removal percentage of nickel ions at various temperatures with time is shown in Fig. (4). At best pH value of (5), the removal percentage of nickel ions decreased with time up to a maximum value after (10) min to be zero after (120) min, and in the other hand Fig. (5) Shows that the removal efficiency of the nickel ions was decreased with time from 97.6 % after 10 min to zero after 120 min and this is occurred at best favorite temperature 35 ^{o}C. Therefore, the effect of the biosorption time is very important because a bed was made by a biosorbent material (algae particles), which it will gradually be saturated with time and lose their ability to absorb nickel ions after 120 min [24].

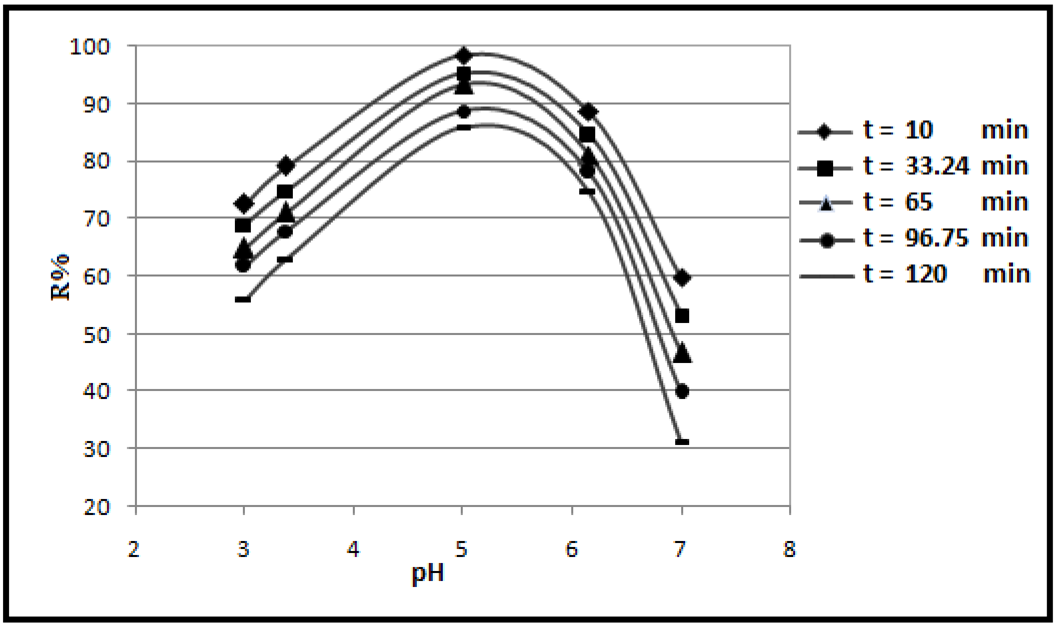

Fig. 3, Effect of pH on the removal percentage of nickel ions at different times

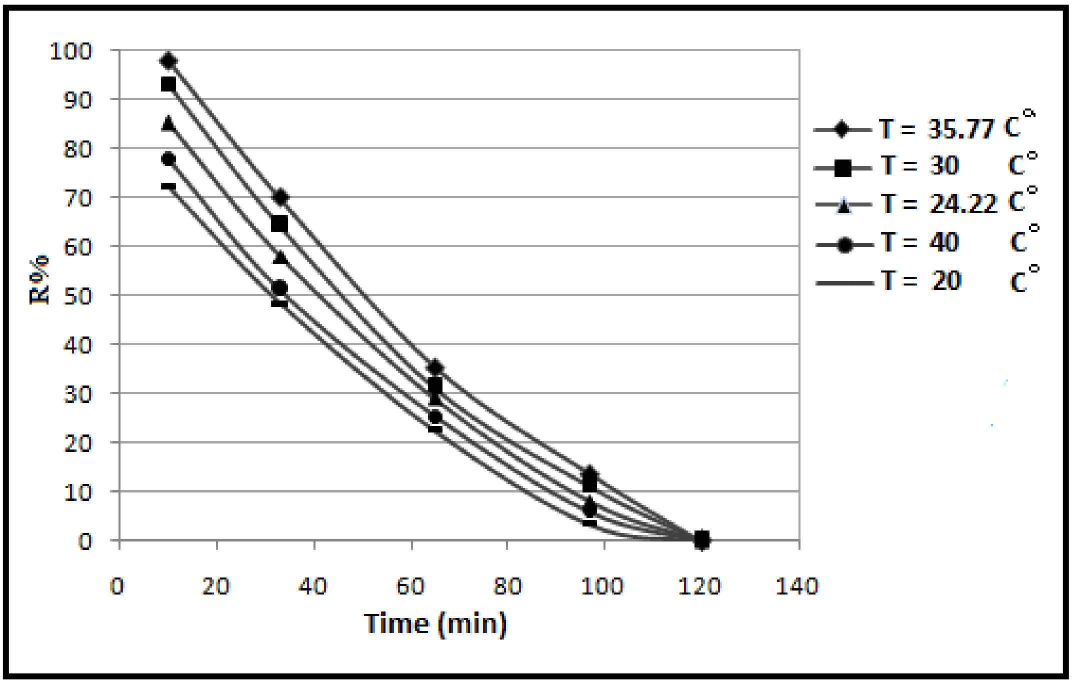

Fig. 4, Effect of time on the removal percentage of nickel ions at different temperature

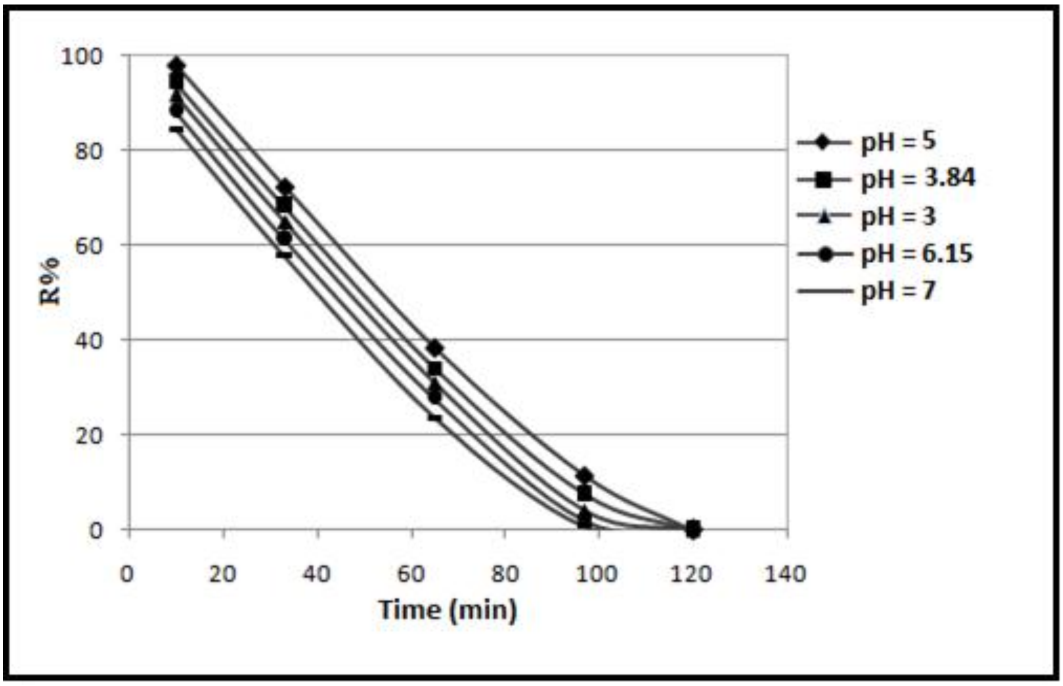

Fig. 5, Effect of time on the removal percentage of nickel ions at different pH

Conclusions

A bed of biosorbent material (*a Laminaria saccharina*) algae can remove the nickel ions from wastewater in a good efficient. Effects of the experimental parameters such as (temperature, pH and time) are very important in the biosorption process. The relationship between the removal percentage and above parameters is shown in equation (5).

The highest removal efficiency of nickel ions obtained was (98.8)%, at optimum operating conditions as follows: - Temperature (35) C^{o}, pH value (5) at time (10) min.

References

1. Nocito F., Lancilli C., Giacomini B., and Sacchi G. A., (2007), "Sulfur Metabolism and Cadmium Stress in Higher Plants", Plant Stress, Global Science Books, Vol. 1, No. 2, pp. 142-156.
2. Aslam M., Hassan I., Malik M., and Matin A., (2004), "Removal of copper from industrial effluent by adsorption with economical viable material", EJEAF Che, Vol. 3, No. 2, pp. 658-664.
3. World Health Organization, (2010), "Guidelines for drinking Water Quality", Geneva, (1984). Res., Vol. 4, No. 2, pp. 281-288.
4. Arsalani N., Rakh R., Ghasemi E., and Entezami A., (2009), "Removal of Ni(II) From Synthetic Solutions Using New Amine-containing Resins Based on Polyacrylonitrile", Iranian Polymer Journal, Vol. 18, No. 8, pp. 623-632.
5. Aslam M.Z., Ramzan N., Naveed S., and Feroze N., (2010), "Ni (II) Removal by biosorption using ficus religiosa (peepal) leaves", J. Chil. Chem. Soc., Vpl.55, No. 1, pp. 81-84.
6. Keane M. A., (1998), "The removal of copper and nickel from aqueous solution using Y zeolite ion exchangers", Colloids Surfaces A: Physicochem. Eng. Aspects, Vol. 138, pp. 11–20.
7. Dermentzis K., Davidis A., Papadopoulou D., Christoforidis A., and Ouzounis, K., (2009), "Copper removal from industrial wastewaters by means of electrostatic shielding driven electrodeionization", Journal of

Engineering Science and Technology Review, Vol. 2, No. 1, pp. 131-136.
8. Rengaraj S., Kim Y., Joo C., Choi K., and Yi. J., (2004), "Batch Adsorptive Removal of Copper Ions in Aqueous Solutions by Ion Exchange Resins: 1200H and IRN97H", Korean J. Chem. Eng., Vol. 21, No. 1, pp. 187-194, .
9. Munoz R., Guieysse B., (2006), " Algal–bacterial processes for the treatment of hazardous contaminants: a review", Water Res. 40: 2799–2815.
10. Volesky, Biosorbent Materials, BiotechnoI. Bioeng Symp., 16: 121-126.
11. Mehta S. K., and Gaur J. P., (2005), "Use of Algae for Removing Heavy Metal Ions from Wastewater: Progress and Prospects Critical Reviews in Biotechnology", J. Hazard Materials, 25 (3) 113 – 152.
12. Davis A., Volesky B., Mucci A., (2003), " A review of the heavy metals biosorption by brown algae", J Water Res 37:4311-4330.
13. Naja G., Vanessa M., Volesky B., (2010), " Biosorption, metal, encyclopedia of industrial biotechnology: bioprocess, biosepration, and cell technology", Wiley, New York.
14. Davis T., Volesky B., Mucci A., (2003), "*A review of the biochemistry of heavy metal biosorption by brown algae*", Water Research, 37(18), 4311- 4330.
15. Sun B. C., Yeoung-S. Y., (2006), "Biosorption of cadmium by various types of dried sludge: Anequilibrium study and investigation of mechanisms", Journal of Hazardous Materials B138, 378–383.
16. Fourest E., Volesky B., (1997), "Alginate properties and heavy metal Biosorption by lamenarine algae ", Appl Biochem Biotechnology, 67, P. 33-44.
17. Sprynskyya M., Buszewski B., Terzyk A.P., and snik J. N., (2006), "Study of the selection mechanism of heavy metal (Pb2+, Cu2+, Ni2+, and Cd2+) adsorption on clinoptilolite" , Journal of Colloid and Interface Science, Vol. 304, pp. 21–28.
18. Davis D.L., (1963), "Design and Analysis of Industrial Experiments", *2nd Ed., Oliver and Boyd*, London.
19. Saleem M., Pirzada T., Qadeer R., (2007), "Sorption of acid violet 17 and direct red 80 dyes on cotton fiber aqueous solution., Colloids Surf, A Physicochem Eng. Asp 292:246-250.
20. Meena AK., Mishrr GK., Rai PK., Rajagopal C., Nagar PN., (2005), " Removal of heavy metal ions from aqueous solution using carbon aerogel as an adsorbent", J Hazard Mater, 122:161-170.
21. Ahmed S., Mustafa T., (2008), " Biosorption of cadmium(II) from aqueous solution by red algae (*Ceramium virgatum*): equilibrium, kinetic and thermodynamic studies", J Hazard Mater, 157:448-454.
22. Jinbai Yang, (1999), "Biosorption of uranium and cadmium on Sargassum seaweed biomass Ph.D. Thesis, McGill University, Departement of Chemical Engineering, Canada.
23. Romera E., Gonzalez F., Ballester A., Blazquez Munoz JA, (2007), "Comparative study of heavy metals using different types of algae", J Bioresour Tech 98:3344-3353.
24. Mehta S. K., and J. R., (2002), "Use of Algae for Removing heavy metal Ions from wastewater progress prospects, p. 432.