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The Removal of Zinc from Aqueous Solutions Using Malvaparviflora

Ahlam Mohammed Farhan ***Rasha Abed Jassim***
Nafeesa J. Kadhim

Department of Chemistry, College of Science for Woman, University of Baghdad, Baghdad, Iraq

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Abstract

In this study, the adsorption of Zn $(NO_3)_2$ is carried out by using surfaces of malvaparviflora. The validity of the adsorption is evaluated by using atomic absorption Spectrophotometry through determination the amount of adsorbed Zn $(NO_3)_2$. Various parameters such as PH, adsorbent weight and contact time are studied in terms of their effect on the reaction progress. Furthermore, Lagergren's equation is used to determine adsorption kinetics. It is observed that high removal of Zn $(NO_3)_2$ is obtained at PH=2. High removal of Zn $(NO_3)_2$ is at the time equivalent of 60 min and reaches equilibrium,where 0.25gm is the best weight of adsorbant . For kinetics the reaction onto malvaparviflora follows pseudo first order Lagergren's equation.

Key words: Zn $(NO_3)_2$, Malvaparviflora, Adsorption, Removal.

Introduction

The following processes are similar to the chemical manufacturing: metal finishing and electroplating major sources of poisonous metals are industrial wastes. The increasing levels of heavy metals discharged to the environment represent a severe threat to human health, living resource and ecological system. According to the World Health Organization (WHO), the toxic metals are aluminum, chromium, magnesium, iron, nickel, cobalt, copper, cadmium, zinc, mercury and lead. Adsorption is one of the most frequent methods used to remove heavy metal ions from several aqueous solution[1].

Malvaparviflora belongs to the family Malvaceae. A hot poultice prepared from leaves is used in treating wounds and swellings. Moreover, it is incorporated into a lotion to treat bruised and broken limbs [2].

Xhosa people of South Africa have used the leaves of M. for drawing swollen, inflamed purulent wounds [3].

The methanolic segment of polyphenols plant is an antioxidant potential for containing different quantities of phenols, flavonoid, saponin, alkaloid, resin and tannin[4].

The removal of Zn(II) from aqueous solutions by studying the optimization variables include: contact time, PH and temperature . The adsorption process can be evaluated by freundlich isotherms. The order of adsorption is evaluated from the kinetic study.

Materials and Methods:

Apparatus:

1- Atomic Absorption Spectrophotometer.
2- Centrifuge type (Remi and R laboratory Centrifuge).
3- Analytical balance type (Sartorious BL 2105).
4- Shaker type SATUART (Great Britain).

Materials:
Preparation of Adsorbent: The powdered malvaperviflora is washed and dried at 5^oC then grinded into particle sizes (150µm).
Adsorbate:
Metal ion (Zinc nitrate hydrate [Zn $(NO_3)_3.6H_2O$] from BDH).
Distilled water is used for dilution.

Adsorption Method:
The adsorption of Zn^{+2} is studied by using a batch equilibration execution is repeated by taking of 25 ml of Zn(NO3)2 solution of concentration 25ppm which is treated with 0.25 g sample of malvaperviflora. Eight conical flasks of the duplication for 2 hours are shaken. Then eight conical flasks are discarded at 3300 rpm for 20 min and the concentration of Zn ions residual in solution is made by Atomic Absorption Spectrophotometer.
The different temperatures (25,35 and 45^oC) affect the adsorption rate. All the every samples (4, 8, 12, 16 and 20) mg/L are shaken for 1 hour. The five samples are centrifuged at 3300 rpm for 20 mins ,then the concentration of Zn+2 ions residual in solution is deliberated by Atomic Absorption Spectrophotometer.

The different influences of PH(3,7 and 10) on adsorption of $Zn(NO_3)_2$ on malvaperviflora
The PH is adjusted by using 0.1M(HCl or NaOH) solution before the adsorption process. The final PH is recorded by the PH meter .Three samples are shaken for 1 hour, samples are centrifuged for 20 min at 3300 rpm than the concentration of Zn^{+2} ions remaining in solution is measured by using Atomic Absorption Spectrophotometer.

Results and Discussion

The effect of Contacton Time: Adsorption equilibrium studies are performed with an adsorbent quantity of (0.25 gm) by 25 ml of $Zn(NO_3)_2$ (25 ppm). The experimental results of adsorption of $Zn(NO_3)_2$ on malvaperviflora at different times (15, 30, 45, 60, 75 and 90)min are illustrated in Fig.1.and Table (1). They show that the adsorption process exhibit an immediate rapid adsorption and reaches equilibrium within a short period of 60 min[5].

Table (1) The Values of Qe and Ce at Different Time for 25 ppm of $Zn(NO_3)_2$ Solution at 298K.

Time /min.	C_e/mg.L^{-1}	Q_e/mg.g^{-1}
15	20.58	0.5525
30	17.69	0.91375
45	13.28	1.465
60	10.81	1.7737
75	10.81	1.7737
90	10.81	1.7737

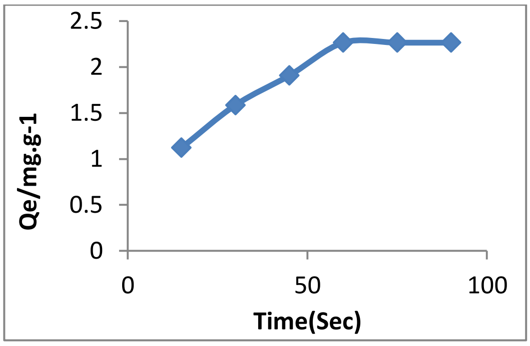


Fig.(1)The Variation of Qe with the Contact Time for 25 ppm of $Zn(NO_3)_2$ Solution at 298K.

Table (2) and Figure (2) show the data and linear relationship between frunendlich isotherm between log Q_e and logC_e a various concentration of $Zn(NO_3)_2$ solution at (298,308 and 318) K.

Table (2) The Value of C_o,C_e and C_e/Q_e, log C_e and log Q_e for the Adsorption of Series Zn $(NO_3)_2$ Solution at(298,308 and 318)K

Temperature (K)	C_O/ mg.L^{-1}	C_e/ mg.L^{-1}	Q_e/ mg.g^{-1}	log C_e	log Q	C_e/Q_e /g.L^{-1}
298K	4	3.71	0.029	0.606	-1.5376	12.79
	8	4.857	0.3143	0.686	-0.5026	15.45
	12	9.1428	1.5857	0.9610	0.2002	5.76
	16	8.4285	1.6572	0.9257	0.4193	5.08
	20	5.5714	1.9428	0.9430	0.5884	2.86
308K	4	3.02	0.098	0.480	1.0087	3.081
	8	6.15	0.185	0.788	0.732	3.324
	12	10.75	1.425	1.0314	0.1538	7.543
	16	9.357	1.564	0.9711	0.1943	5.982
	20	9.071	1.593	0.9576	0.2021	5.695
318K	4	3.19	0.081	0.503	1.091	3.938
	8	2.714	2.23	0.434	0.348	1.22
	12	2.000	2.3	0.301	0.362	0.87
	16	0.214	2.48	0.67	0.394	0.086
	20	0.143	2.49	0.84	0.395	0.057

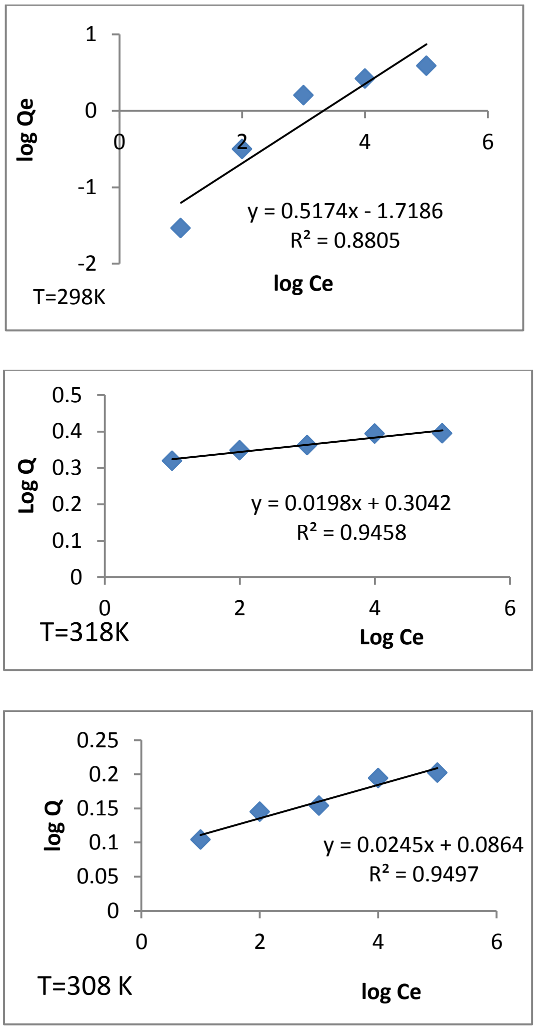


Fig.(2) Freundlich linear Relationship between log Q and log C_e for a Series $Zn(NO_3)_2$ Solution at Different Temperatures .

The linearised form of the Freundlich equation [6] is as follows:

log Q = log K_f+ 1 / n log Ce ----- (1)

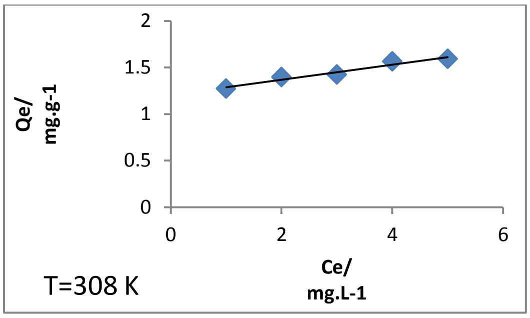
The Freundlich isotherm constants K_f and 1 / n can be calculated from the plot between log Qe and log Ce Fig.(2) where Ce: Equilibrium is the adsorbate concentration (mg/L), C_o:Initial adsorbate concentration put in contact with the adsorbent (mg/L) and Qe: Amount adsorbate adsorbed at the equilibrium (mg / g). K_f (mg / g), 1/n (L / g) and n are the Freundlich constants.

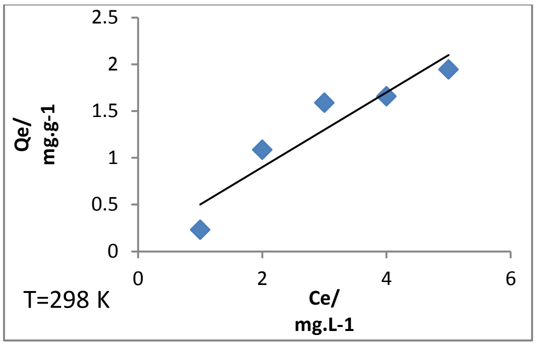
Figure (2) shows the relationship of frunendlich data, therefore frunendlich parameter determined in this work is included in Table (3)

Table(3) The Freundlich Constants at Different Temperatures.

T(K)	Log K_f	K_f mg/g/(L/g)	1/n	n	R^2
298	-0.732	5.395	0.284	3.521	0.896
308	0.086	1.219	0.024	41.66	0.949
318	0.304	2.013	0.019	52.63	0.945

Figure (3) give the relationship Q_e vs.C_e for the adsorption a series of $Zn(NO_3)_2$ solution at different temperatures .According to Giles classification ,the shape of adsorption isotherms obtained in this work is like L-type isotherm. This could be explained, as the concentration of $Zn(NO_3)_2$ whish increases the vacant sites on the surface that are filled with the $Zn(NO_3)_2$ molecules in completion with the water molecules and there is monolaver adsorption of $Zn(NO_3)_2$ on Malva parviflora[7]





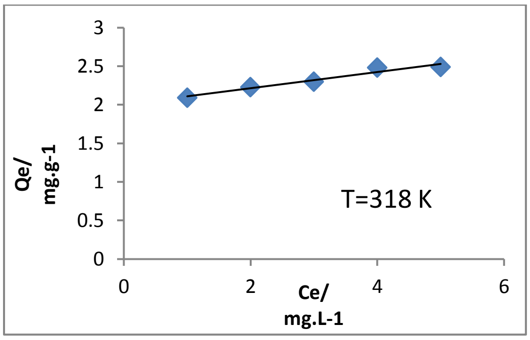


Fig.(3) The Plot of Q_e against C_e for the Adsorption a series $Zn(NO_3)_2$ Solution at Dfferent Temperatures .

Effect of PH

The PH solutionaffect the charge of surface, the adsorbent, the degree of ionization. The new types of the adsorbate .The adsorption of metal ions from aqueous solution depends on the PH solution[8]. The removal of metal ions when pH varies from 3-10 by adsorption experiments use different PH methods. PH affects the adsorption of Zn (II) on adsorbent are shown in Figure(4) and Table (4). From Figure 5 it can be seen clearly that the maximum adsorption occurs at lower PH value namely (3). This may be due to the presence of a large number of H^+ ions which in turn neutralize the negatively charged adsorbent thereby reducing hindrance to the diffusion of Znic ions. The decrease at high PH may belong to abundance of OH^- ions causing hindrance to diffusion Znic[9].

Table (4) The quantity of adsorption at different pH value, using malvaparviflora at 318K for 25ppm Zn $(NO_3)_2$ solution.

pH	Q_e/mg.g^{-1}	C_e/mg.L^{-1}
3	1.265	12.35
7	0.69	18.071
10	0.229	22.71

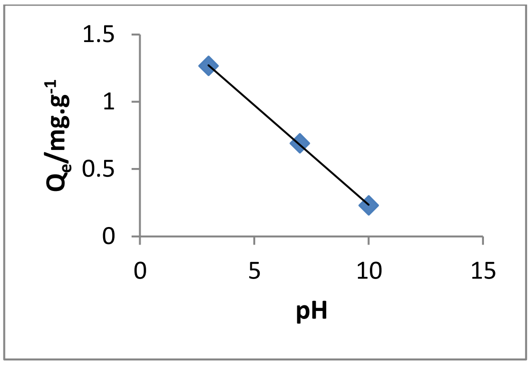


Fig. (4)The Quantity of Adsorption at Different PH value Using Malvaparviflora at 318K for 25ppm Zn $(NO_3)_2$ Solution

Thermodynamics Functions:

The thermodynamic functions ΔH^o, ΔG^o, and ΔS^o have been calculated by using the following formulas

ΔG^o =- RT ln K ------------------------ (2)

l n K = - ΔH^o /RT + constant -------- (3)

$\Delta G^o = \Delta H^o - T\Delta S^o$ --------------------- (4)

According to Eq.(2,3 and 4)the $\Delta H^o$and ΔS^o parameters for $Zn(NO_3)_2$ can be calculated from the slope and intercepts of the plot of In(K) versus 1/T (Fig. 5)where K is the thermodynamic equilibrium constant of adsorption process. K, can be calculated form intercept of linear equation log Qve. log C_e The calculated values of ΔH^o, ΔS^o, and ΔG^o are listed in Table 5.

Table (5)The Thermodynamic Function of the Adsorptin Process .

T(K)	ΔG^o ($kJ.mol^{-1}$)	ΔS^o ($J.mol^{-1}.K$)	ΔH^o*10^{-2} ($kJ.mol^{-1}$)
298	-7.606	25.816	-8.721
308	-5.966	19.653	
318	-2.252	7.356	

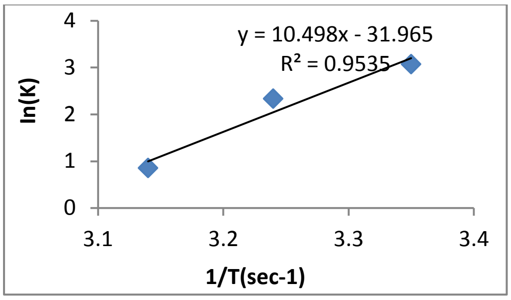


Fig.(5)The Plot of ln K vs.the Reciprocal of Temperature .

The obtained values for Gibbs free energy change (ΔG^o) ranging from (-7.606 to - 2.252) KJ/mole for $Zn(NO_3)_2$ adsorption on malvaperviflora ranging from (298- 318) K. The negative ΔG^o values indicate the thermodynamically spontaneous nature of the adsorption. The reduction in ΔG^o values with increasing temperature shows a decrease in feasibility of adsorption in higher temperatures. The value of the parameter ΔH^o is -0.08721 KJ/mole for $Zn(NO_3)_2$ adsorption on malvaperviflora. The positive ΔH^o is an indicator of exothermic nature of the adsorption and also its magnitude gives information on the type of adsorption, which can be either physical or chemical. The enthalpy of adsorption, ranging from 7.356to 25.816 J/mole corresponds to a physical sorption. The adsorption heat of $Zn(NO_3)_2$ is in range of physisorption. Therefore, the ΔH^ovalues show that the $Zn(NO_3)_2$ adsorption on adsorbent is takes place via physisorption[10].

Adsorption Kinetics

The adsorption kinetics of $Zn(NO_3)_2$ on malvaperviflora adsorbents is investigated to determine the order of reaction. The bkinetic equations applied can be expressed as follows [11]:

1-Langergren model

Pseudo first order Lagergren's is as follows

log ($q_e - q_t$) = log qe $-k_1$ / 2.303 t---- (5)

where qe and qt (mg/g) are the sum of adsorbed $Zn(NO_3)_2$ at equilibrium and time t. k_1 is the first order rate constant (min^{-1}). The plot of log (q_e-q_t) versus t for the adsorption of $Zn(NO_3)_2$ onto malvaperviflora is drawn in Figure (6) and Table (6), while the values of k_1 and qe are calculated from the slope and then intercept. The resulted R^2 value is high (0.953) which signifies that the adsorption of $Zn(NO_3)_2$ perfectly complies with pseudo first order reaction. Similar kinetic results have also been reported for the adsorption of certain dyes onto Aspergillusniger and onto Peat [5].

Table(6) Kinetic Parameters (Langergren model) of Removal $Zn(NO_3)_2$ by Malvaperviflora .

Time (min.)	q_t	q_e	lnq_e-q_t
15	11.214	22.643	2.4361
30	15.857		1.9148
45	19.0715		1.2729
60	22.643		0
75	22.643		0
90	22.643		0

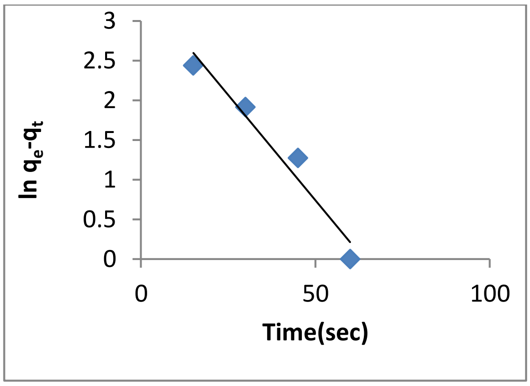


Fig.(6) The Lagergren Model for $Zn(NO_3)_2$ of 25 ppm at 298K Surface

2-Morris- Weber model:

The effect of intraparticle diffusion resistance on the adsorption can be determined by the following relationship [12]:

$q_t = k_D t^{1/2}$ (6)

Where k_D is the diffusion rate constant(mg/g min), which can be determined from the slope of the linear plot of qt versus $t^{1/2}$. Fig. (7) presents a linear fit of this model for adsorption of $Zn(NO_3)_2$.

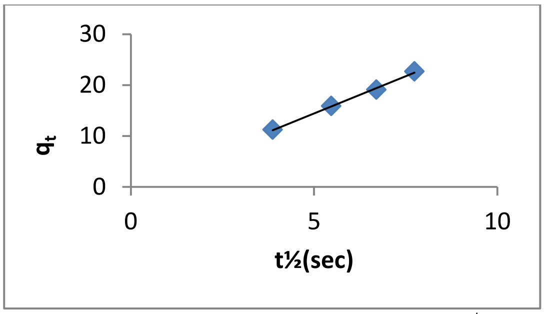


Fig.(7) The plot of qt against √t for adsorption $Zn(NO_3)_2$of 25ppm on malvaperviflora at 298K .

3- Rauschenberg Model

This kinetic model is proposed to discuss the behavior of much adsorption process in solution and Rauschenberg has introduced following formula [6] :-

$F = [1\text{-}6 /\pi^2]\ e\text{-}B_t$ .... (7)

$Bt = -\ 0.4977 - Ln\ (1\text{-}F)$ .... (8)

$F = q_t / q_e$ .... (9)

Plotting of time values versus B_t revealed a linear relationship with relatively acceptable R^2 values. Fig.(8) shows the variation of B_t with the time for 25 ppm of $Zn(NO_3)_2$ at temperature constant. According to this model characterizes the rate determining mechanisms for the diffusion process of Zn^{+2} ions from the bulk solution to the absorbent surface and absorption occurred.

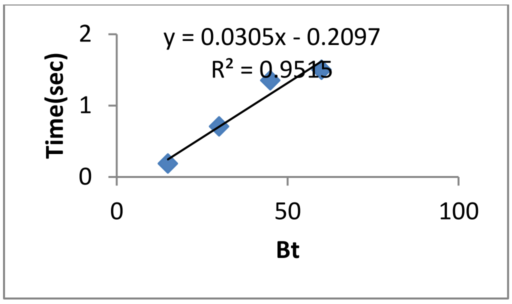


Fig. (8) The Vriation of Bt with Time for $Zn(NO_3)_2$ of 25ppm on Malvaperviflora at 298K .

References:

[1] Al-Najar, J. A.; Ramzy, S. H. and Zaydoon, M. S. 2010. Removal of Cadmium(II) Onto Granular Activated Carbon and Kaolinite Using Batch Adsorption, Eng. and Tech. Journal, 28(10):2070 .

[2] Shale, T. L.; Stirk, W. A. and van Staden, J. 1999. Screening of medicinal plants used in Lesotho for anti-bacterial and anti – inflammatory activity .J Ethnopharmacol, 67(3):347-354.

[3] Watt, J. M. and Brandwijk, M. G. 1962. The medicinal and poisonous plants of southern and eastern Africa:being an account of their medicinal and other uses ,chemical composition pharmacological effects and toxicology in man and animals .E and S Livingstone(Ltd.).

[4] Rammal, F. H.; Hijazi, H. A. and Badran, H. B. 2012b.Preliminary phytochemical screening and extraction of polyphenol from stems and leaves of a Lebanese plant Malvaparviflora L. Int J Curr Pharm Res., 4(1):55-59.

[5] Hamaza, M. O. and Kareem, S. H. 2012. Adsorption of Direct Yellow 4Dye on the Silica Prepared From Locally Available Sodium Silicate, Eng. And Tech Journal, 30(15):2609-2625.

[6] Kadhim, N. J. 2012. Adsorption Study for Trifluralin on Iraqi α-

Alumina, J. Baghdad for Sci.,9(1)153-159.

[7] Khaled Eldurini, N. M.; Abdulkader, S. S. and Ziad, A. M. 2010. Adsorption of Carbaryle and Benomyl from Water by Jordanian Bentonite, Al-Mustansiriya J, 21(2)79-88.

[8] Teker, M. and Imamoglu, M. 1999. Kinetic and thermodynamic study of Cr (II) and Mn (II). adsorption on some commercial adsorbents, Turk J Chem.23(13), 185 – 19.

[9] Olayinka, K. O.; Alo, B. I. and Adu, A. 2007. Kinetic and thermodynamic study of Cr (II) and Mn (II) adsorption on some commercial adsorbents, J. Applied for Sci.,7 (16),2307- 2313.

[10] Ahmed, M. J.; Tamer, S. K. and Mohammed, A. H. A. 2012. Adsorption of phenol and P-Nitro phenol onto date stones: Equilibrium Isotherms, Kinetics and Thermodynamics Studies, Eng. Journal, 18(6)743-761.

[11] Mckay, Y. S. and Ho. G. 2000 .The kinetic of sorption of divalent metal ions on to sphagnum moss peat, Journal of IWA, 34(3): 735-742.

[12] Weber, W. J. and Morris, J. C. 1962. Advances in water pollution research: removal of biologically resistant pollutant from waste water by adsorption, in Proceedings of the International Conference on Water Pollution Symposium, 2(4): 231–266.

إزالة الزنك من المحاليل المائية باستخدام نبات الخباز

احلام محمد فرحان **رشا عبد جاسم** **نفيسه جبار كاظم**

قسم الكيمياء، كلية العلوم للبنات، جامعة بغداد، بغداد، العراق

الخلاصة:

تم في هذا البحث دراسة امتزاز $Zn(NO_3)_2$ على سطح نبات الخباز و قياس سرعة الامتزاز باستخدام جهاز قياس المطيافية الذرية من خلال تحديد كمية $Zn(NO_3)_2$ الممتزة .كما تم دراسة العديد من العوامل المؤثرة في سرعة التفاعل ومنها : الدالة الحامضية ،وزن السطح الماز وزمن التلامس بالإضافة الى ذلك تم استخدام معادلة Lagergren لتحديد حركيات الامتزاز.

حيث لوحظ انه اعلى ازالة $Zn(NO_3)_2$ كانت عند pH=2 و زمن التماس للوصول الى التوازن عند (60 دقيقة) وافضل وزن (0,25غرام).اما بالنسبة لحركيات الامتزاز فان التفاعل كان من الرتبة الاولى الكاذبة معادلة Lagergren على سطح نبات الخباز.

الكلمات المفتاحية: نترات الزنك، نبات الخباز، عملية الامتزاز، عملية الازالة.