# Efficiency of Tea Disposal from Cafeteria for Removal Nickel ion from Contaminated Groundwater

**Rusul Nasser Mohammed**

*Department of chemical Engineering, College of Engineering, University of Basrah*

Rusul.mohamed@uobasrah.edu.iq

## Abstract

This work aims to study the removal of Nickel from ground water using low cost adsorbent tea waste from cafeteria. The total adsorbed amounts, equilibrium uptakes and overall removal efficiency of Nickel were determined by investigating the breakthrough curve obtained at different inlet Nickel concentrations, various pH value, gain size of waste tea and bed height. Decrease in the grain size of adsorbent tea from 0.3 to 0.05 cm resulted in essential increase in the removal rate and total adsorbed amounts while increasing the bed depth leads the increase of bed capability and the breakthrough period. The experimental data were calibrated using three isotherm models, Dubinin- Radushkevich (DRM) Langmuir (LM) , Freundlich (FM) where the experimental data is well fitted to the Langmuir (LM). Experimental and theoretical breakthrough study showed that the prolonged breakthrough period and maximum capability of nickel is achieved at pH of 3, 125 mg/L of inlet concentration and 0.5 m of bed depth. As a final engineering observation, waste tea from cafeteria is a good and low-cost material that can absorb nickel from groundwater.

**Keywords:** Adsorption, Waste tea , Nickel removal, Groundwater

## الخلاصة

تهدف الدراسة الى البحث في ازالة النيكل من المياه الجوفية باستخدام مخلفات الشاي المتوفرة محليا" . البحث تناول من الناحية العملية دراسة الامتزاز للمادة المستخدمة في البحث للنيكل مع مختلف الظروف التشغيلية والتي تضمنت تركيز النيكل الابتدائي، قيمة الرقم الهيدروجيني، حجم دقائق الشاي وارتفاع الحشوة المستخدمة في برج الامتزاز . من الناحية النظرية هناك ثلاث موديلات رياضيه , Dubinin Radushkevich– Freundlich , Langmuir تم استخدامها للتحقق من النتائج العملية حيث اثبتت النتائج ان موديل Langmuir مثل الامتزاز بشكل تام حيث ان الموديل تطابق بشكل جيد مع النتائج العملية. ان هذه الدراسة اثبتت ان مادة الشاي له قدره عالية على امتزاز النيكل عند الظروف المثلى وهي 3 للأس الهيدروجيني ، 125 ملغم /لتر لتركيز النيكل الابتدائي و 0.5 م لارتفاع حشوة ماده الامتزاز . كما وجد ان زيادة نسبة الإزالة الى 50% مع زيادة كمية المادة الممتزه الى 218 ملغم من الممكن ان تتحقق بتقليل حجم دقائق الشاي من 0.3 الى 0.05 سم وزيادة ارتفاع الحشوة . من ذلك نستنتج ان مخلفات الشاي ممكن ان تستخدم لامتزاز النيكل من المياه الجوفية وبكلف واطئة جدا" .

**الكلمات المفتاحية** : أمتزاز ، اوراق الشاي المتبقي، ازالة النيكل ، المياه الجوفيه

## Introduction

Pollution of groundwater by heavy metal is one of the major ecological complications owing to the fast automation. Dissolved heavy metals in the Aqueous discharges of the industries may have effects on the environment (Hegazi *et.al.* 2013; Kadirvelu *et.al.*, 2013 ). Nickel ion is one of these metals, it has an essential rate in the luster manufacturing and production of nickel cadmium (cd) strings. It is also used in large quantities in leather treating, cement, film making and in dye manufacturing (Bilal *et.al.*, 2013 ). The high exhaustion of nickel and its yields is produced into wastwater, which produces various sicknesses and disorders such as heart, kidney disease, lung fibrosis, increment the danger of nasty tumors, fast respiration, torso pain and bad health (Adedirin *et al*., 2011; Malkoc, *et al*., 2014 ; Shinde *et al*., 2012) . Consequently, nickel concentration into sewage water needs to be treated. Acceptable ranges of nickel in drinking water are 10-2 ppm, as it is selected by World Health Organization (WHO) while higher. The Traditional ways for heavy metals removal from ground water and sewage have insufficient efficiencies at little metal concentrations of (1–100) mg/L .

Moreover,these methods containing several process such as chemical rainfall, electrolysis, solvent withdrawal,thickening,ion exchange,membrane filtration and piosorption, (Ghaedi *et.al*., 2014; Roosta, *et.al.,* 2014 ; Roosta *et.al.,* 2011),which are expensive and can create toxic sludge (Pahlavanzadeha *et.al.,* 2010 ). In recent years, another research has been used microorganisms for nickel removal (Rodrigues *et.al.,* 2012) investigated the nickel absorption onto dehydrated biomass spirulina platensis and Chlorella vulgaris. This investigation has been found that the two bacteria types are capable of removing nickel, but are more useful in removing lead (pb) and zinc (zn). Recently, the researcher investigated and analyzed nickel removal using zeolites and predicted the removal rate by artificial neural network (ANN) technique (Turp *et.al.,* 2011).The agriculture wastelands are used for helping in limitation rate of the physical and chemical treatment technologies (Lehmann *et.al*., 2011).Most of these studies have been depended on batch kinetic for adsorbing metal ions. Nevertheless, adsorption process in the fixed bed is considered the main adsorption technical. The dynamic performance of a fixed-bed adsorption can be investigated based on the breakthrough profile for designing the adsorption column. There are several economical metals were used to adsorb the heavy metal from groundwater. In this study, a large quantity of tea waste from cafeteria is used for the removal of Ni from groundwater and the objectives of this work were to (1) investigate the probability of using tea waste from cafeteria as a material for removing Ni using a laboratory scale fixed-bed column.(2) Determine the higher values of adsorption capability based on several isotherm models, Langmuir (LM),Freundlich (FM) and Dubinin- Radushkevich (DRM).(3) Determine the influence of operation parameters such as bed length, grain size of tea bed, alkalinity and influent nickel concentration by predicting the breakthrough curves using Thomas Model.(4) Find out the probability of using tea as an adsorbent for nickel absorption by Thermodynamics parameters and equilibrium isothermal.

## Material and Methods

### Chemicals preparation

The stock solution was prepared from 1000 mg/L of nickel. Then, it was treated with fresh water to the required concentration. 1 M of mixture hydroxyl sodium hydraulic acid (HCl) solutions was added to the last solution for adjusting the alkalinity of feed concentration. Nickel quantity in deposit was examined by the standard complex metric method (Lehmann *et.al*., 1999; Gu, *et.al*., 1984).

### Adsorbent Preparation

The tea waste was collected from cafeteria . Before the experiments operation, the tea waste was washed twice with tap water .Then, it was dried at 75 Co overnight and stored in polythene luggage for experiments. Physical absorption process was performed in this study and all tea waste properties waste is shown in Table 1.

**Table 1: Characteristics of Tea waste from cafeteria**

| | |
|---|---|
| Water soluble constituents (%) | 6.09 |
| Unsolvable materials (%) 51.5 - 64.62 | 80.24 |
| Moisture (%) | 10.99 |
| Ash (%) | 2.2.97 |
| Total loss of explosion (%) | 95.08 |
| Bulk density (g/cm$^3$) | 0.113 |
| Grain size (mm) | 0.5 −3 |
| Surface area BET (m$^2$/g) | 0.38 |
| The bed porosity | 0.48 |
| Conductivity (ms/m$^2$) | 276.75 |

## Experiments Batch and Fixed-bed Column

Effects of operating factors, such as adsorbent potion, inlet nickel concentration was investigated during batch experiments which is implicated in 250 mL tapering bottles employed in a $H_2O$ bath shaker and surprised at 360 rpm. Each tapering bottle stunned for period from 2– 90 min. Before mixing operation, 5 mL sample were taken from mixture solution. $NiCl·_6HO$ was an investigative chemical prepared in deionized water. Three values of inlet nickel concentrations (25, 125 and 250 mg/L) were selected to study the influence of feed concentration on removal rate. The column absorption was made from perspex tubes of 50 cm total length filled with total bed depth and 3 cm internal diameter. In a typical experiment the metal of a recognized application was forced at a fixed discharge using a peristaltic pump (Cole Parmer, USA) with recognized bed depth of waste tea adsorbent. The grain size of waste tea was selected from 1.0 to 3.0 mm. After exhaustion 95 percent of bed capacity, the adsorption process was finished. The temperature of feed solution was adjusted at 27 ∘C using thermostatic bath.
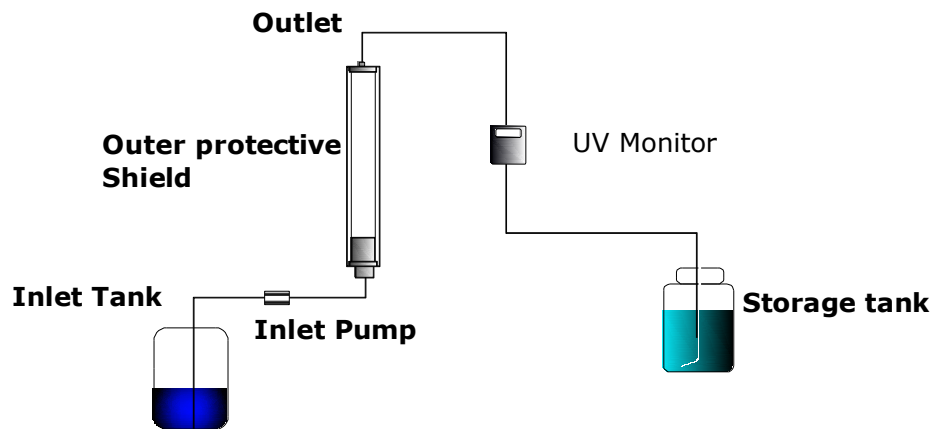


**Figure 1: diagram of absorption column for Nickel removal**

## Mathematical model

The experimental data were calibrated using three mathematical models: Dubinin-Radushkevich (DRM in eq.3) Langmuir (LM in eq.1), Freundlich (FM in eq. (2) because adsorption isotherms study is very useful to observe the characteristic of adsorbent apparent and the similarity of tea to Ni concertation (Chen *et al*., 2004 ).

$$\frac{1}{q_A} = \frac{1}{Q} + \left(\frac{1}{KQ}\right)\left(\frac{1}{C_A}\right) \qquad \text{... (1)}$$

The second model used in this work is Freundlich model (FM) whereas the general form of the adsorption equation is (Gautham *et al*., 2012 ):

$$q_A = Ḱ_f(C_A)^{\frac{1}{n}} \qquad \text{... (2)}$$

$$Ln\ q_A = Ln\ q_{max,DR} - K(\varepsilon)^2 \quad \text{... (3)}$$

Where $q_A$ is the adsorption capability at Equilibrium in (mgram/gram). $C_A$ is the concentration of material, $K'$ is the energy factor , K in (E in kJ/mol) are equal to $E = 1/(2K)^{1/2}$ , ε is defined Polanyi potential , $q_{max,DR}$ the maximum adsorption capability based on the second model ( in mgram/gram) .

**Predicting the Breakthrough profile using Thomas model**

The influence of operation parameters was investigated based on the breakthrough profile. The breakthrough profile is commonly stated in terms of adsorbed component concentration or regularized concentration (Dada *et al.,* 2012 ) .

## Control of external film resistance (EFR)

Derivation of the adsorption described by Langmuir model explained that the uptake rate is equal to the rate of adsorption minus desorption rate (Tongbao *et al*., 2004 ). Thus for the adsorption of solute A :

$$\frac{\partial C_s}{\partial t} = k_a C(\acute{Q} - C_s) - k_d C_s \qquad\qquad \ldots (4)$$

where;

$$\acute{K} = k\_a/k\_d \; \& \; \acute{Q} = ((1 + \acute{K}C\_o)/(\acute{K}C\_o)) \; C\_s^\wedge\infty \qquad \ldots (5)$$

By substituting $\acute{Q}$ in equation Eq. (5),

$$\frac{\partial\left(C_s/C_s^\infty\right)}{\partial t} = k_a \frac{1 + \acute{K}C_o}{\acute{K}} \left[\frac{C}{C_o}\left(1 - \frac{C_s}{C_s^\infty}\right) - \frac{1}{1 + \acute{K}C_o}\frac{C_s}{C_s^\infty}\left(1 - \frac{C}{C_o}\right)\right]$$

In Langmuir kinetics concept, Eq. (4) can be rewritten as:

$$\frac{\partial\left(C_s/C_s^\infty\right)}{\partial t} = \Delta_a \left[\frac{C}{C_o}\left(1 - \frac{C_s}{C_s^\infty}\right) - r^* \; \frac{C_s}{C_s^\infty}\left(1 - \frac{C}{C_o}\right)\right] \qquad\qquad \ldots (6)$$

where ;

$\Delta_a = k_a \frac{1 + \acute{K}C_o}{\acute{K}}$ and $r^* = 1/(1 + \acute{K}C_o$ At (EFR) controlling :

$$\frac{\partial C_s}{\partial t} = \frac{k_f a}{1 - \epsilon}[C - C_i] \qquad\qquad ..(7)$$

when the rate of adsorption is equal to zero, $C = C_i$ and $\frac{\partial\left(C_s/C_s^\infty\right)}{\partial t} = 0$ . Also, by substituting Eq. (7) into Eq. (6) ,

$$C_i = \frac{C_s}{C_s^\infty} \frac{r^* C_o}{1 + \left(C_s/C_s^\infty\right)* (r^* - 1)} \ldots \qquad\qquad (8)$$

According to the definition of $C_i$ , Eq. (4) can be rewritten as:

$$\frac{\partial\left(C_s/C_s^\infty\right)}{\partial t} = \frac{k_f a* C_o}{C_s^\infty * (1 - \epsilon)\left[1 + \left(C_s/C_s^\infty\right)* (r^* - 1)\right]}\left[\frac{C}{C_o}\left(1 - \frac{C_s}{C_s^\infty}\right) - r^* \frac{C_s}{C_s^\infty}\left(1 - \frac{C}{C_o}\right)\right] \ldots (9)$$

**Control of internal Particle Resistance (IPR) (Tongbao *et.al., 2004* ).**

The rate of adsorbate uptake is expressed as:

$$\frac{\partial C_{As}}{\partial t} = k_s a \; (C_{Asi} - C_{As}) \qquad\qquad ..(10)$$

since , $\frac{\partial C_s}{\partial t} = k_s a \; (C_{si} - C_s) \quad \ldots \qquad\qquad (11)$

$$C_{si} = \frac{C_s^\infty}{(r^* - 1) + r^* \left(C_o/C\right)} \qquad \ldots \qquad\qquad (12)$$

The differential equation in this case can be obtained by substituting Csi instead of $C\_s$ in Eq. (6) and substituting the relationship into Eq. (10).Therefore (Tongbao *et al.,* 2004 );

$$\frac{\partial\left(C_s/C_s^\infty\right)}{\partial t} = \frac{k_s\,a}{\left[r^* + \left(C/C_o\right)(r^* - 1)\right]}\left[\frac{C}{C_o}\left(1 - \frac{C_s}{C_s^\infty}\right) - r^*\,\frac{C_s}{C_s^\infty}\left(1 - \frac{C}{C_o}\right)\right] \quad \ldots(14)$$

$$\frac{\partial\left(C_s/C_s^\infty\right)}{\partial t} = \Delta_s\left[\frac{C}{C_o}\left(1 - \frac{C_s}{C_s^\infty}\right) - r^*\,\frac{C_s}{C_s^\infty}\left(1 - \frac{C}{C_o}\right)\right] \quad \ldots(15)$$

**3.2.2 Combined internal and external resistances:**

For the case in which both the external film resistance and intraparticle resistance are important, the previous rate equations may be combined together according to (Anthony *et al.,* 1985 ). since the total rate of adsorbate uptake is equal to the total sum of all rate equations, then it may be shown that:

$$\frac{\partial\left(C_s/C_s^\infty\right)}{\partial t} = \left[\frac{k_f\,a\,C_o}{C_s^\infty(1-\epsilon)\left[1 + \left(C_s/C_s^\infty\right)(r^* - 1)\right]} + \frac{k_s\,a}{\left[r^* + \left(C/C_o\right)(r^* - 1)\right]}\right]\left[\frac{C}{C_o}\left(1 - \frac{C_s}{C_s^\infty}\right) - r^*\,\frac{C_s}{C_s^\infty}\left(1 - \frac{C}{C_o}\right)\right] \quad \ldots(16)$$

Where

$$\Delta = \left(\frac{k_f\,a\,C_o}{C_s^\infty(1-\epsilon)\left[1 + \left(C_s/C_s^\infty\right)(r^* - 1)\right]}\right) + \left(\frac{k_s\,a}{\left[r^* + \left(C/C_o\right)(r^* - 1)\right]}\right)$$

Eq. (14) can be expressed by defining the bed-length and the time parameters (Anthony *et al.,* 1985 ).The dimensionless groups are:

$$Bl = \frac{Z(1 - \epsilon)C_s^\infty\Delta}{\epsilon\,U_z C_o} \quad \ldots(17)$$

$$\vartheta = \Delta\Theta = \Delta\left(t\vartheta - \frac{Z}{U_z}\right) \quad \ldots(18)$$

$$\overline{Q} = \frac{C_s}{C_s^\infty} \quad \ldots(19)$$

$$\overline{X} = \frac{C}{C_o} \quad \ldots(20)$$

where;

Bl: Bed-length parameter and

$\vartheta$: Time parameter

Br substituting the dimensionless parameter into Eq.14 the result as:

$$\frac{\partial\overline{Q}}{\partial\vartheta} = \overline{X}(1 - \overline{Q}) - r^*\,\overline{Q}(1 - \overline{X}) \quad \ldots(21)$$

A computer program was written in Matlab 7.0 language as it is shown in figure (2) to simulate the adsorption process in fixed bed column based on the combined internal and external resistances.
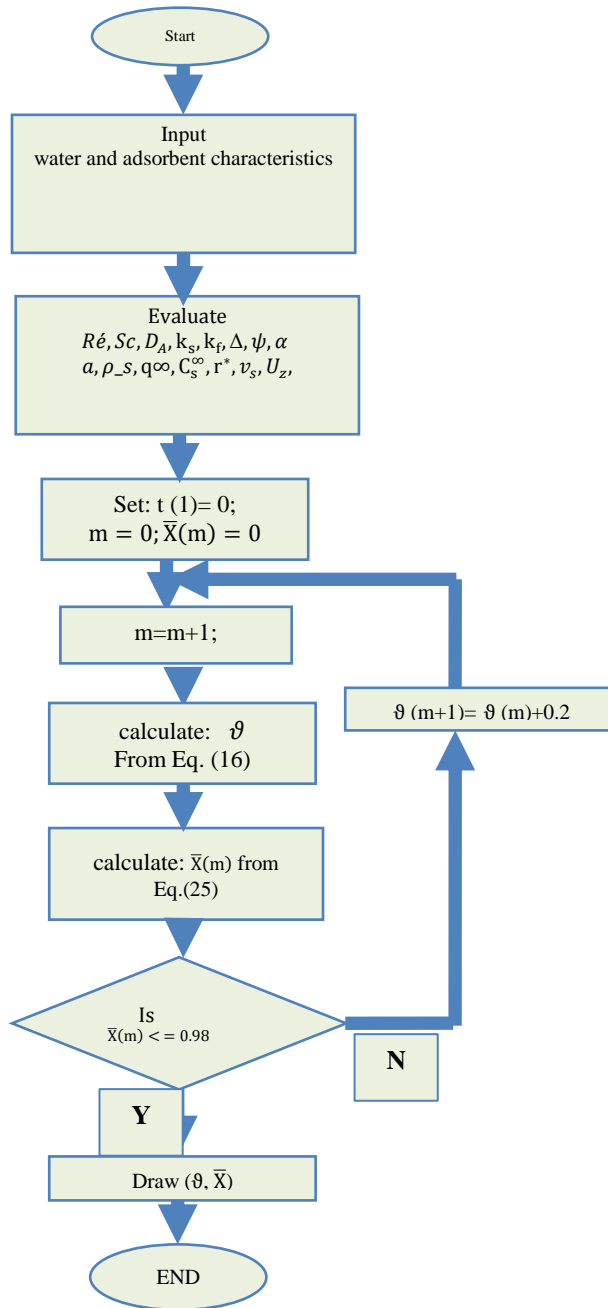
Start

Input
water and adsorbent characteristics

Evaluate
$Ré, Sc, D_A, k_s, k_f, \Delta, \psi, \alpha$
$a, \rho\_s, q\infty, C_s^\infty, r^*, v_s, U_z,$

Set: t (1)= 0;
$m = 0; \overline{X}(m) = 0$

m=m+1;

$\vartheta (m+1)= \vartheta (m)+0.2$

calculate: $\vartheta$
From Eq. (16)

calculate: $\overline{X}(m)$ from
Eq.(25)

Is
$\overline{X}(m) < = 0.98$

N

Y

Draw $(\vartheta, \overline{X})$

END

**Figure 2: Flow chart of for Nickel removal**

## Results and Discussion

### Spectroscopic Analysis

Absorption of heavy metals by inorganic bio martial with involvement of functional groups was investigated recently in (Namasivayam *et.al.*, 2002 ).The numbers of absorption peaks was noted by Fourier transform infrared spectral (FTIS) analysis of tea excess, which indicated to the complicity of tea adsorbent nature towards different metal spices. The FTIS spectrum of tea ((see Fig. 3)) showed the infrared spectra data after its transferring to Microsoft Excel ( ME) program by Perkin-Elmer Spectrum (PES). It can be seen readily from this data that there are numbers of absorption peaks that

demonstrating the difficult environment of the component tested. The FTIS spectroscopic analysis showed that the gangs detected at about 1333 was allocated -SO$_3$ stretching group. The greatest value of 1100 cm$^{-1}$ indicated the existence of another groups while the C-N stretching groups were noted in the range of 520 cm$^{-1}$ . It was revealed that the greatest value was observed at 4100 cm$^{-1}$ that could be assigned to – OH groups. The gangs noticed at 3500–3503 cm−1 were assigned to the aliphatic C–H group. The peak around 1640 -1636 cm−1 characterize to the stretch of C- O. The insignificant peaks in the region of 1502 cm$^{-1}$ is represented by amine group. The methane symmetric vibration was detected at the peaks of 1400 and 1477 cm−1. This result showed that the type of useful group is compiled to the metal compulsory (Yunus *et.al.,* 2008).. It can be seen readily in table 2, the difference result before and after tea adsorption which identified that the groups C- O stretching, the bonded hydroxide, minor amine group and the similarity in the bending of methane were particularly complicated in Ni metal separation (Sheng *et.al.,*2005). It was showed that the larger difference in the recurrence rate was -23 cm$^{-1}$ as it was observed the minor amine group .

**Table: 2  Fourier transform spectroscopy analysis for Ni removal by tea waste**

| Beak No. | Recurrence Rate (1/cm)[a] | Recurrence Rate (1/cm)[b] | Variation | Task |
|---|---|---|---|---|
| B1 | 520 | 520 | 0 | -CN stretching |
| B2 | 1100 | 1100 | 0 | C-O stretching of ether groups |
| B3 | 1333 | 1330 | -3 | -SO3 stretching |
| B4 | 1400 | 1402 | 2 | Symmetric bending of methane |
| B5 | 1477 | 1470 | -7 | Symmetric bending of methane |
| B6 | 1520 | 1543 | -23 | minor amino group |
| B7 | 1640 | 1636 | -4 | C-O starching |
| B8 | 2900 | 2901 | 1 | Aliphatic (Ap) C-H group |
| B9 | 3500 | 3503 | 3 | Aliphatic(Ap) C-H group |
| B10 | 4100 | 4094 | -6 | Bounded extending |

**a :  before adsorption of Ni (II)   ;   b : after  adsorption of Ni (II)   .**
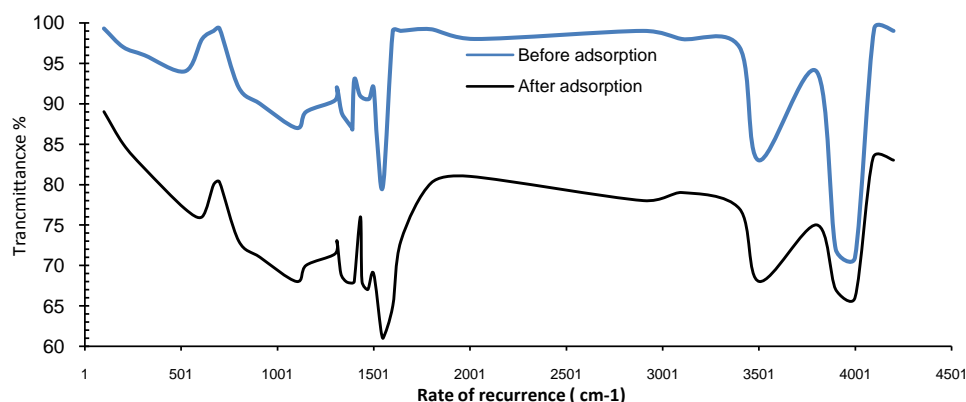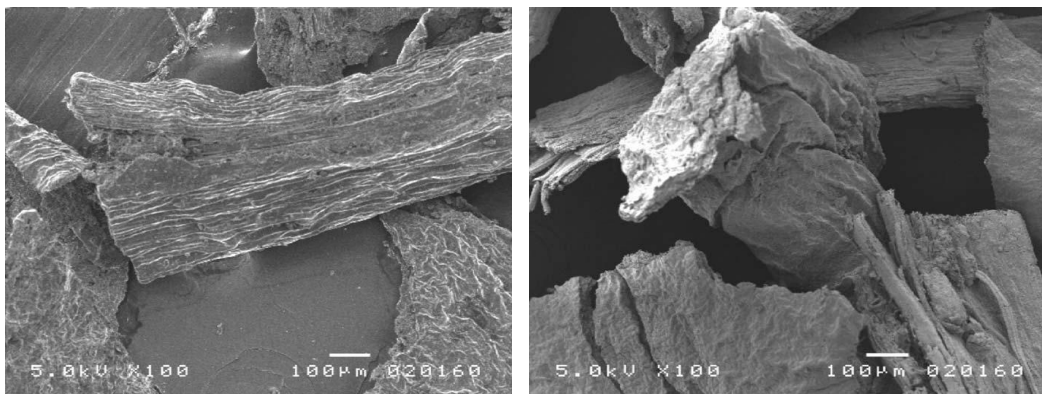


**Figure 3:  Spectroscopic analysis of tea waste before and after adsorption.**

(a) Before                    (b) after
**Figure: 4 SEM Micrograph**

## Thermodynamic and Equilibrium Isothermal results

Table (3) illustrates the model isotherm parameters and correlation factors ($R^2$) at different operating temperatures.  It was illustrated that the maximum adsorption capability is observed by Langmuir model (LM) of 7.03 mgram/gram at 40 $C^o$. The separation process was more advantageous at higher temperatures, as revealed in the b constant increasing.  Nickel amount found by Langmuir model (LM) is the best value based on the other models , as the $R^2$ values were nearly (0.996). The result of the second model (FM) obtained the advantageous adsorption when all the n values were greater than one. For the third model (DRM), the E values are in the range of 10– 16 kJ/mol, approving that ion interchange is founded in nickel metal. The highest value of adsorption capability observed in this work was compared with other investigator works based on the first model (Langmuir model LM). The result showed the maximum tea waste capability was higher than adsorbent palm shell activated carbon (Tanweer *et.al.,* 2011; Villaescusa *et.al.,*2005) corncobs adsorbent (Ali *et.al.,*2014), Walnut sawdust (Olayinka,*et.al.,*2009), and soybean hulls modified with citric acid were higher. Nevertheless there were lower than coconut husk adsorbent (Marshall *et.al.,*1999) due to dissimilar properties of each adsorbent metal . As a result, tea waste could be used as a good adsorbent for nickel separation from groundwater as  its $q_{max}$ value was higher than the other metals.

The thermodynamic factors (Tf) of energy change ($\Delta G^0$), entropy ($\Delta S^0$) and enthalpy change (ΔH0)  were  calculated from Eqs. (28) and (29), respectively.

$$\Delta G^0 = R\,T\,lnb \qquad ... (28)$$
$$\ln b = \Delta H_o / R\,T + \Delta S / R \qquad ... (29)$$

where R is the  vapor constant and  T is the degree of temperature in (Co). Table (4) shows that all values of $\Delta G^0$ were negative at different temperatures while $\Delta H^0$  value was positive owing to the endothermic nature of separation process. The entropy value ($\Delta S_0$) was positive at different temperature and constant at (137.5) (J/ kmole) due to the increasing of arbitrariness at the interface of solid with solution during the adsorption of Nickel by tea metal.

## Fixed-bed Column Study

Operation of continuous process in fixed bed is so beneficial for absorbing the pollutants from ground water. It is used in different chemical productions due to their good adsorption capability and easy to carry out (Di *et.al.,*2008) .The operation in the

packed column is not reach 12 column continuously while during batch process, the adsorbent and adsorbate are in contact until equilibrium state is achieved. The chief design factors such as column bed height, initial concentration, pH of solution, and grain size of waste tea will be studied using fixed-bed column study.

**Table: 3 Model isotherm parameters at variant temperatures**

| Equilibrium model | Parameters | Value | Temperature (C°) |
|---|---|---|---|
| Freundlich (FM) | $Ḱ_f$ | 3.14 | 30 |
| | n | 4.81 | |
| | $R^2$ | 0.788 | |
| | $Ḱ_f$ | 3.63 | 35 |
| | n | 4.25 | |
| | $R^2$ | 0.96 | |
| | $Ḱ_f$ | 3.92 | 40 |
| | n | 4.41 | |
| | $R^2$ | 0.97 | |
| Langmuir (LM) | Q | 6.01 | 30 |
| | b | 31000 | |
| | $R^2$ | 0.97 | |
| | Q | 6.71 | 35 |
| | b | 39000 | |
| | $R^2$ | 0.999 | |
| | Q | 7.03 | 40 |
| | b | 41100 | |
| | $R^2$ | 0.996 | |
| Dubinin- Radushkevich (DRM) | $q_m$ | 22.31 | 30 |
| | E | 13.9 | |
| | $R^2$ | 0.965 | |
| | $q_m$ | 24.61 | 35 |
| | E | 13.230 | |
| | $R^2$ | 0.987 | |
| | $q_m$ | 25.25 | 40 |
| | E | 73.91 | |
| | $R^2$ | 0.982 | |

**Table 4: Thermodynamic factors for removal Nickel at different temperature**

| Temperature (C°) | $ΔG^0$ (J/mole) | ΔH0 ((J/mole) | ΔS (J/Kmole) |
|---|---|---|---|
| 30 | −25750 | 15880 | 137.5 |
| 35 | − 26540 | - | - |
| 40 | − 27160 | - | - |

## Influence of initial alkalinity

The alkalinity of the feed is important design factor in the piosorption process as it effects on the chemistry of any component in water and adsorbent apparent metal

required sites (Gu *et.al.,*1984)   . Table 5 showed the effect of solution pH (ranged between 1 to 5) and the size of tea particle on adsorption.  In adsorption of Nickel by tea waste from cafeteria, the highest value of bed capability with prolonged breakthrough period is obtained at pH of  3 .  It was noted that the removal rate is increased as pH increased. The proposed observation from this explanation  is that  the positive value of hydrogen ion contest with Nickel component on the external layer of the adsorbent that would delay Nickel ions from reaching to  the necessary sites of the sorbent . At pH of  5, the Nickel ions raised due to the speeding of hydroxide anions formed on nickel hydroxide . Thus, the maximum pH value was designated and fixed on 3.  The hydroxyl group is so effective required sites for component ion, which produce fixed complex by organization. It was noted that the interface layer between the useful groups in waste tea and nickel causes the increasing of alkalinity in the first step. Later, pH decreased when the capability of the bed in the column proceeds.  For the inlet solution with pH 1, 2, 3 and  5.0, the outlet pH sharply increased to 3.2, 4.1, 4.9 and 5.8, respectively. The increasing of effluent pH may result from desorption of hydrogen ion (H +) from the mixture and dissolution of various foams from the adsorbent external layer. Dried microbial usually involves one of two chemical alterations while no dried microbial typically includes light component like potassium (K), sodium (Na) and calcium ( Ca). In the dried state, the microbial is countered with an aqueous mixture of a high concentration of Ni in order to measure the sites of calcium or potassium (Hawari et al.,2005 ). Table 5 shows the total adsorbed nickel quantities, nickel removal efficiency onto tea absorbent related to the solution pH and the equilibrium nickel uptakes. It was depicted, although the quantity of total adsorbed nickel raised with increment of alkalinity from 2.0 to 4.0. The removal efficiency (31.68 %) was greater at pH 3 then pH of one, two, and five which were (46.16, 18.23 and 33.94), respectively of the total nickel applied to the column. Figure (5) shows the influence of alkalinity on removal rate. It can be seen readily that there is a respectable contract between the theoretical values and experimental data whereas the minimum value of correlation coefficient result at pH 1 of 0.922.

## Effect of grain size of adsorbent

Table 5 and Figure 6 show the effect grain size of adsorbent. The experiments were carried out for three various grain sizes:  0.05, 0.1, and 0.3 cm, under constant flow rates (0.6 L/hr) and inlet nickel concentration (125 mg/L). The tea weight of adsorbent was taken as 0.012, 0.011, 0.01 and 0.0035 mg to clear completely drops of 20 cm, 0.05 cm, 0.1 and 0.3 cm, respectively. It was observed that the increasing of grain dimension of tea adsorbent decreases both the breakthrough time and the maximum bed capability.  The performance of adsorption is better with small grain dimensions, but the small grain causes to raise of flow resistance of the column. Concerning various grain size, higher bed capability and breakthrough period  at 0.3, 0.1, and 0.05 mm grain size were 0.57  , 12.78  and 18.05, mg/g and 260, 320 and, 450 min, respectively. It was observed that higher rate of adsorption was achieved at a smaller grain size of 0.05 cm because the smaller grains have a shorter diffusion path that led to penetrate the adsorbate into the tea gain rapidly. Table (5) shows that the removal rate decreased with increasing grain sizes where high removal efficiency of 46 % was attained at small grain of 0.5 mm. In addition, the experimental data coincided with the predicted result whereas the correlation coefficients for the height of (0.05-0.3) cm were between 0.81 and 0.93. It can

be seen readily, the experimental data was close to Thomas model. The values of k from Thomas model at grain size of tea, 0.05, 1 and 0.3, were $3.16 * 10^{-6}$, $5.67 *10^{-6}$ and $2.5 * 10^{-6}$ L/mg . min, respectively.

**Table 5: Influence of most important design parameters on the total adsorbed quantity**

| Grain Size(cm) | $C_o$ | pH | H (bed) mm | $q_{eq}$ (mg/g) | $q_{total}$ (mg) | Removal Efficiency (%) | Correlation Coefficient [a] |
|---|---|---|---|---|---|---|---|
| 0.3 | 125 | 1 | 500 | 3.43 | 25.55 | 18.23 | 0.922 |
| 0.3 | 125 | 2 | 500 | 7.56 | 71.35 | 33.97 | 0.962 |
| 0.3 | 125 | 3 | 500 | 11.45 | 114.61 | 41.24 | 0.971 |
| 0.3 | 125 | 5 | 500 | 9.23 | 92.56 | 31.68 | 0.973 |
| 0.1 | 125 | 3 | 500 | 19.34 | 218.66 | 46.16 | 0.811 |
| 0.1 | 125 | 3 | 500 | 13.85 | 150.64 | 43.87 | 0.893 |
| 0.3 | 125 | 3 | 500 | 10.44 | 98.74 | 44.89 | 0.947 |
| 0.3 | 25 | 3 | 500 | 8.41 | 77.87 | 47.49 | 0.978 |
| 0.3 | 250 | 3 | 500 | 12.22 | 118.32 | 30.43 | 0.989 |
| 0.3 | 125 | 3 | 100 | 11.43 | 47.88 | 31.81 | 0.922 |
| 0.3 | 125 | 3 | 300 | 12.66 | 72.27 | 34.43 | 0.953 |
| 0.3 | 125 | 3 | 500 | 14.87 | 116.32 | 40.7 | 0.982 |

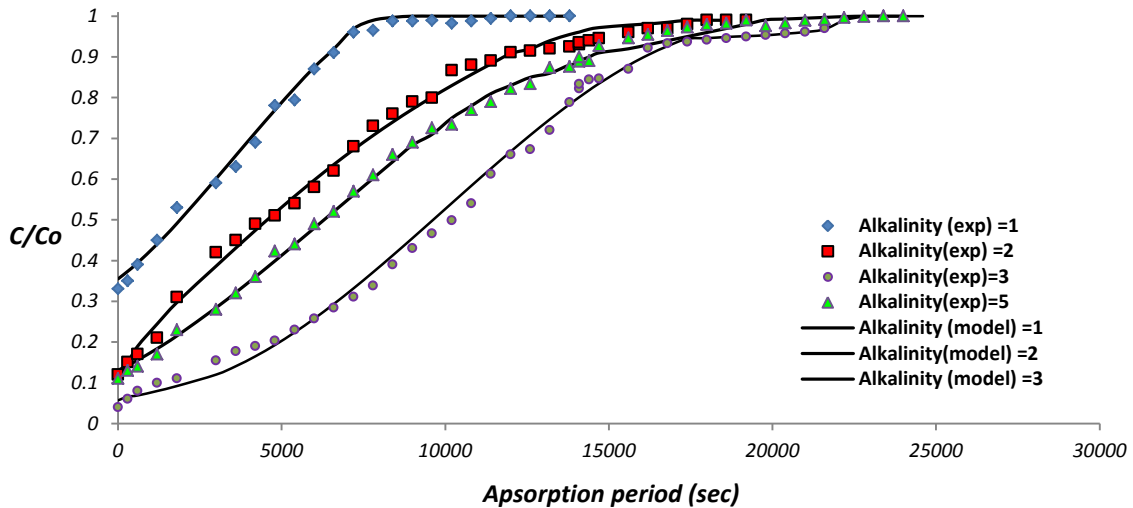a; Correlation coefficient is found by Thomas model



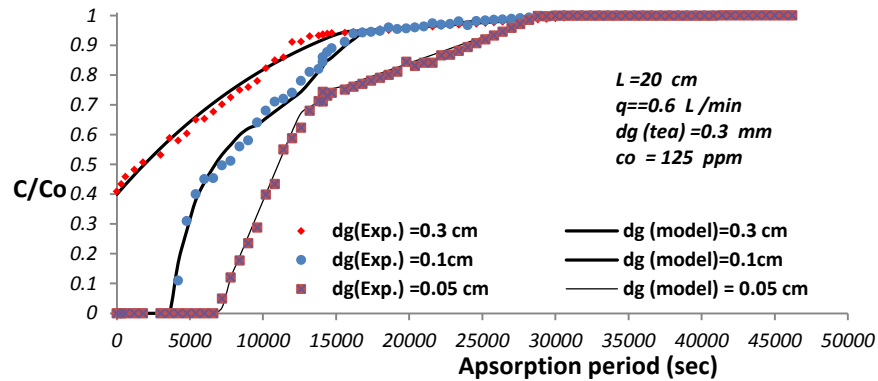**Fig. 5 The Experimental and Thomas modeled results for nickel removal at different pH values**

**Figure 6 : The Experimental and modeled results for Nickel removal at various grain size (0.5, 1, and 3 mm)**

## Influence of inlet concentration

This research investigate the influence of inlet nickel concentration because it provides a significant driving force to incredulous the mass transfer resistance of component for both phases, solid with liquid. This experiment is carried out while the other operating parameters are kept constant of 3 mm of grain size, 20 cm of bed length and 3 of pH value. The increment of the initial concentration of Nickel from 25 to 250 ppm which has significant effect on the breakthrough profile whereas the adsorption bed capability was increased from 8.41 to 12.12 m gram/gram and the time shorted to 350 min (Figure 7). The proposed explanation from this observation is that the fixed bed of tea was saturated rapidly at the highest concentration of 250 mg/L that cause to short the breakthrough profile and the short adsorption time. When the inlet concentrations decrease to 25 mg /L, the breakthrough profile was delay with small value of removal rate (47.49 %) owing to reduction of diffusion coefficient. Moreover, the sharp breakthrough profile was resulted with 250 ppm of inlet nickel as shown in table 5. There is a good contract between the experimental and theatrical results whereas the correlation coefficients ($R^2$) for inlet concentration (25-250) mg/l were between 0.893 and 0.989. It was observed from Figure (6), the experimental data of breakthrough profile were very closely to Thomas model. The k value of Thomas model at inlet concentration of tea, 250, 125 and 25, were 2 *10-6, 3.6*10-6 and 6 *10-6   L/mg.min, respectively.
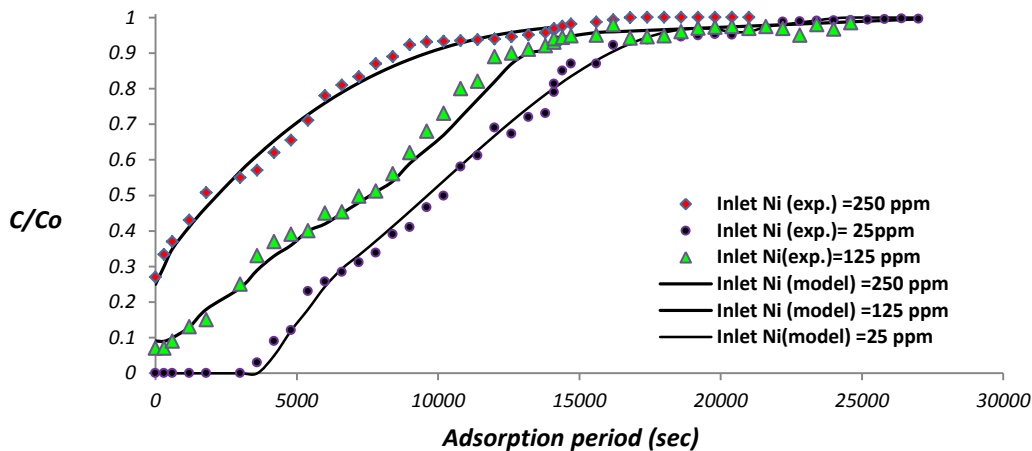


**Figure 7: The Experimental and model results for Nickel removal at various initial concentrations**

## Influence of bed height

Figure 8 shows the effect of bed height on the removel nickel rate. Different weights of waste tea (4.5, 8.5 and 11.5 g of were taken to produce 100, 300 and 500 mm of bed height, respectively. the discharge and inlet concentration were assumed to be practically constant during this experiments. The results depicted that the breakthrough period and the bed capability increased as the packed bed increased to 500 mm owing to the increment in adsorbent amounts that will produce higher driving force. The higher value of bed capability for different bed depth 100, 300 and 500 mm were 11.57, 12.6 and 14.8 mg/g, respectively. Furthermore, tea capability for Ni removel increased with the increment of height bed due to availability of more binding situates for adsorption. The correlation coefficients for all bed depth (0.5-3) m were between 0.81 and 0.93 that certain the similarity between the experimental and predicted data. The values of k at bed depth of tea, 0.1, 0.3 and 0.5, were $2.16 * 10^{-6}$, $3.4 * 10^{-6}$ and $5.6 * 10^{-6}$ L/mg .min, respectively that it is calculated based on Thomas model. The nickel removal efficiency increased from 32.8 to 40.7% as the bed height increased from 0.1 to 0.5 m. The detention time of the liquid in the column increased when the bed length increased that led to diffuse the tea particles through the porosity of the adsorbent. Thus, the media capability must be variable with the operation period.
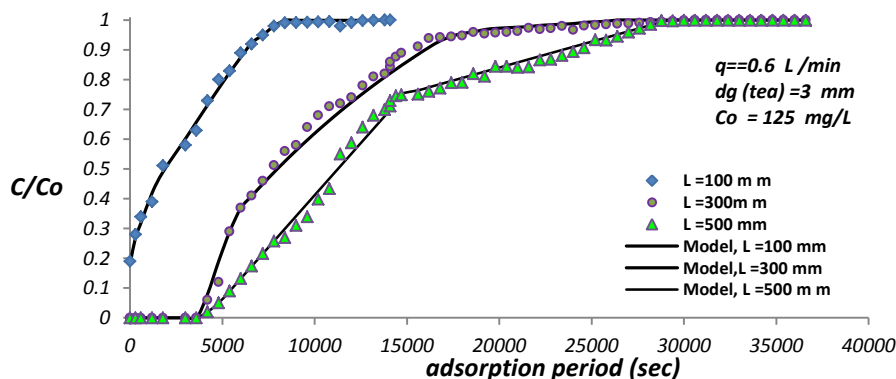


**Figure 8: Experimental and Thomas model results for Nickel at various bed heights**

## Conclusion

Nickel metal was removed from ground water using waste tea from cafeteria. The conclusion from the experiment is given below:

1. Spectroscopic analysis concluded that, carbon–hydrogen;–hydroxyl and carbon–hydrogen groups were the main useful groups of tea cafeteria.
2. The batch experiments concluded, that nickel adsorption is increased with the increasing the number of adsorption sites. The equilibrium metal uptake of nickel decreased with the increment of inlet nickel concentration.
3. The change of thermodynamic factors (Tf) enthalpy, energy and entropy were studied. The nickel adsorption at various temperatures were natural when the values of energy change to less than zero. All values of enthalpy change were larger than zero that indicated to the endothermic nature of adsorption.
4. The experimental data were calibrated using three isotherm models, Dubinin-Radushkevich (DRM) Langmuir (LM) , Freundlich (FM) where the experimental data is well fitted to the Langmuir (LM). The higher value of adsorption capability is observed by Langmuir ( LM) of 7.03 mg/g at 40 Co.

5. Thomas model was used for investigating the operating parameter of the fixed bed column, inlet concentration, alkalinity, bed length and grain size of adsorbent.   The prolonged breakthrough period and the higher values of nickel capability is achieved at 3 of feed alkalinity, 125 mg/L of inlet concentration and 500 mm of bed depth . The decreasing of tea grain size from 3 to 0.025 cm causes an increase the breakthrough period. As a final engineering observation, waste tea from cafeteria is a good and economy materiel that can remove nickel concentration from polluted ground water.

## References

Adedirin, O.;  Adamu, U.;  Eddy, O.; 2011. "Biosorption of Cr (VI) and Ni (II) from aqueous solution onto Bacillus subtillis immobilsed in Agarose gel". Der. Chemic. Sinic. 2 (5): 173-188.

Ali S. M.;  Khalid A. R .; Majid R.M .; 2014. " The removal of Zinc, Chromium   and nickel from industrial waste water using Corn cobs".  Iraqi Journal of Science, 55(1) :123-131.

Anthony L. H. and Robert N. Maddox, 1985 "Mass Transfer: Fundamentals and Applications",  Prentice-Hall Inc.: 460.

Bailey, S.E. ;  Olin, T.J.;  Bricka, R.M. ;  Adrian, D.D. 1999. " A review of pontentially low-cost sorbents for heavy metals, Water Res. 33 (11):2469–2479.

Bilal, M.  Shah, Ashfaq T.; J. A.   2013.  "Waste biomass adsorbents for copper removal from industrial wastewater-a review" Journal of Hazardous Materials, 263,( 2) : 322–333

Chen J. P. ; Wu, S. 2004. "Acid/base-treated activated carbons: characterization of functional groups and metal adsorptive properties," Langmuir,  20 (6) : 2233–2242.

Dada, A.O .;  Olalekan, A.P .; Olatunya, A.M.; 2012. "  Langmuir, Freundlich, Temkin and Dubinin–Radushkevich Isotherms Studies of Equilibrium Sorption of Zn2+ Unto Phosphoric Acid Modified Rice Husk. IOSR Journal of Applied Chemistry  , 3: 38- 45.

Di, X.;  Xiaol, T,, Changlun C, Xiangke W.; 2008. " Removal of Pb(II) from aqueous solution by oxidized multiwalled carbon nanotubes ,  Journal of Hazardous Materials 154 , 407–416.

Gautham P. Jeppua, T.;  Prabhakar Clementa .2012 .  " A modified Langmuir-Freundlich isotherm model for simulating pH-dependent adsorption effects" . Journal of Contaminant Hydrology. 129–130 .

Ghaedi, M.a ,;  Ansari, A.b,;  Habibi, M.H.c, Asghari,;  A.R.d; 2014. " Optimization of the ultrasonic assisted removal of methylene blue by gold nanoparticles loaded on activated carbon using experimental design methodology ". Ultrasonics Sonochemistry , 21, (1) : 242-252.

Gu, H. lensoy, 1984. Kompleksometrenin Esasları ve Kompleksometrik Titrasy- onlar, Fatih Yayınevi Matbaası, Istanbul,:. 76–77.

Hawari, A.H.; Mulliga, C.N.; 2005. " Biosorption of lead(II), cadmium(II), copper(II) and nickel(II) by anaerobic granular biomass" . Bioresource Tech neology . 97 : 692–700.

Hegazi, H. A.; 2013. " Removal of heavy metals from wastewater using agricultural and industrial wastes as adsorbent". HBRC Journal, 9 (3): 276–282.

Kadirvelu, Thamaraiselvi, C., K.; Namasivayam, 2001. "Removal of heavy metal from industrial wastewaters by adsorption ontoactivated carbon prepared from an agricultural solid waste" , Bioresour. Technol. 76 : 63–65 .

Lehmann, M.;  Zouboulism, A.I.;  Matis, K.A.; 1999. " Removal of metal ions from dilute  aqueous solutions: a comparative study of inorganic sorbent materials" . Chemosphere (6) : 881-892.

Malkoc, E.; 2011 . Ni (II) removal from aqueous solutions using cone biomass of. J. Hazard. Material  137 (2):  899-908.

Marshall, W.E.; Wartelle,  L.H.  Johns, M.M.;  Toles, C.A.; 1999 . " Enhanced metal adsorption by soybean hulls modified with citric acid".  Bioresoure  Technology, 69: 263–268.

Namasivayam C.; and D. Kavitha, 2002 . " Removal of Congo Red from Water by Adsorption onto Activated Carbon Prepared from Coir Pith, an Agricultural Solid Waste," Dyes and Pigments Journal, 54, :47–58.

Olayinka, O. K. .; Oyedeji, O. A., 2009. "Removal of Cr and Ni ions from aqueous solution by adsorption on modified coconut husk," African J. of Environmental Science and Technology.  3(10): 286-293.

Pahlavanzadeha, H.;  Keshtkarb, A.R.;   Safdarib, J.;  Abadi, Z., 2010" Biosorption of nickel(II) from aqueous solution by brown algae: equilibrium, dynamic and thermodynamic studies" . Journal Hazard. Material ,. 175: 304–310.

Rodrigues, M.;  Ferreira, L.; de Carvalho, J.;  Lodi, A.; 2012."Metal biosorption onto dry biomass of Arthrospira (Spirulina) platensis and Chlorella vulgaris: multi-metal systems" . Jounal  Hazard. Material  : 246–255.

Roosta, M.a,.;   Ghaedi, M.a , ' Daneshfar, A.b, Sahraei, R.b.; 2014. " Removal of malachite green from aqueous solution by zinc oxide nanoparticle loaded on activated carbon: Kinetics and isotherm study ". Journal of Industrial and Engineering Chemistry .20,(1). : 17-28.

Roosta, M.a,;   Ghaedi, M.a ,;   Daneshfar, A.b,;   Sahraei, R.b.; Asghari, A.c Spectrochimica Acta 2014,"Optimization of the combined ultrasonic assisted/adsorption method for the removal of malachite green by gold nanoparticles loaded on activated carbon".  Molecular and Biomolecular Spectroscopy . 118: 55-65.

Sheng, P.X.;   Ting, Y.-P.;   Chen, J.P. Hong, L.; 2005. " Sorption of lead, copper,cadmium, zinc, and nickel by marine algal biomass: characterization of biosorptive capacity and investigation of mechanisms, J. Colloid Interfacial Science , 275:131–141.

Shinde, N.R.;  Bankar, A.V.; Kumar, A.R.;  Zinjarde, S.S.; 2012 . Removal of Ni (II) ions from aqueous solutions by biosorption onto two strains of Yarrowia lipolytica" .J. Environal. Management . 102: 115–124.

Spectrochimica Acta -2014. Part A ,"Experimental design based response surface methodology optimization of ultrasonic assisted adsorption of safaranin O by tin sulfide nanoparticle loaded on activated carbon Molecular and Biomolecular Spectroscopy" , 122, 25 : 223-231.

Tanweer, A.; Mohammad  R.;  Mohammad  R.; 2011.  " The use of date palm as a potential adsorbent for wastewater treatment: a review.  Environ Science Pollutant Research International  . 19(5):1464-1484.

Tongbao C.;  Yi J.' 2004. " Yinping Zhang,  Prediction of breakthrough curves for adsorption on activated carbon fibers in a fixed bed" .Carbon,  42 : 3081–3085.

Turp, S.M.;  Eren, B.; Ates, A.; 2011. " Prediction of adsorption efficiency for the removal of nickel (II) ions by zeolite using artificial neural network (ANN) approach" . Fresenius Environmental Bull. 12: 3158–3165.

Villaescusa,I.; Fiol, N.;  Martinez,M.;   Miralles, J. ; 2005. " Removal of copper and nickel ions from aqueous solutions by grape stalks wastes, Water Research , 38 : 992–1002.

 Yunus P.; 2008.  "Removal of Copper(II) Ions from Aqueous Medium by Biosorption onto Powdered Waste Sludge" , J. PROCESS BIOCHEMISTRY  41(5):1047-1054.