



## Experimental Investigation of Thermodynamics, Kinetics, and Equilibrium of Nickel Ion Removal from Wastewater Using Zinc Oxide Nanoparticles as the Adsorbent

Shurooq T. Remedhan  <sup>a\*</sup>

<sup>a</sup> Department of Chemical Engineering, University of Technology-Iraq. [80024@uotechnology.edu.iq](mailto:80024@uotechnology.edu.iq)

\*Corresponding Author

Submitted: 25/09/2019

Accepted: 23/11/2019

Published: 25/07/2020

### KEY WORDS

ZnO nanoparticles, Ni (II), kinetics, isotherms, adsorption, thermodynamics.

### ABSTRACT

*In the present study commercial zinc oxide (ZnO) nanoparticles in the size of 30 nm were utilized as an adsorbent for the removal of Ni (II) ion from synthetic waste aqueous solution. Adsorption capacity of ZnO for removing Ni (II) ions from aqueous solutions was measured at different pH, adsorbent dose, contact time, temperature and metal ion concentration. Moreover, adsorption isotherms, kinetics and thermodynamics were studied to understand the nature and mechanism of adsorption. ZnO nanoparticles were characterized by X-Ray diffract analysis (XRD), Fourier Transform Infrared Spectroscopy (FT-IR), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and Brunauer-Emmett-Teller (BET). The maximum amount of Ni (II) removal were found to be (98.71%) from its aqueous solutions by ZnO nanoparticles which was achieved at the evaluated optimum conditions. The experimental kinetic data were examined using the pseudo-second-order rate model with a high regression coefficient. The adsorption isotherm was well described to the equilibrium data by Langmuir isotherm model ( $R^2=0.990$ ). In addition, the calculated thermodynamic parameters, the standard Gibbs free energy  $\Delta G^0$ , the change in standard enthalpy  $\Delta H^0$  and the standard entropy change  $\Delta S^0$  showed that the adsorption of Ni (II) onto ZnO nanoparticles was feasible, endothermic and spontaneous respectively. The experimental results suggest that ZnO nanoparticles can be used as a potential adsorbent for the efficient removal of heavy metals from aqueous solutions than any other adsorbent because an economical and low- consumption energy due to its ambient operation conditions.*

**How to cite this article:** Sh. T. Remedhan, "Experimental investigation of thermodynamics, kinetics, and equilibrium of nickel ion removal from wastewater using zinc oxide nanoparticles as the adsorbent," Engineering and Technology Journal, Vol. 38, Part A, No. 07, pp. 1047-1061, 2020.

DOI: <https://doi.org/10.30684/etj.v38i7A.608>

This is an open access article under the CC BY 4.0 license <http://creativecommons.org/licenses/by/4.0>

## 1. Introduction

Industrial effluents are the major sources for contamination of water resources by heavy metals. Treatment of industrial waste water which frequently contains high levels of heavy metals was therefore required before the disposal in order to avoid water pollution[1]. These effluents have a significant impact on the water resources because they contain slowly- or non-biodegradable organic materials. For nickel in industry is a byproduct of the electroplating process, which is non-biodegradable and bio-accumulative [2]. Metal nickel is an essential trace nutrient to all high plants and animals including humans; however, if present in amounts above a permitted level, it can be poisonous and even fatal. According to World Health Organization (WHO) standards, the maximum allowable concentration of Ni(II) in drinking water is 0.07 ppm [3], while the maximum admissible limit in Iraqi standards for nickel ion in residual water that is drained to the water resources and the public sewage are (0.2 and 0.1) ppm respectively [4]. The important sources of nickel metal are mineral processing, electroplating and steam-electric power plants that have toxic effects on human for instance, nickel causes cancer for lung and kidney, distress in gastrointestinal, and skin dermatitis [5]. Several methods, such as coagulation, chemical precipitation, ion exchange, liquid-liquid extraction, electro-dialysis and resins have been developed for the removal of heavy metal ions from industrial wastewater[6]. Each method has its limitations in terms of cost, complexity or efficiency, however, when planning to choose an appropriate technology for heavy metal removal, there are several points which must be taken into account, including the efficiency of the method, generation of secondary waste, and cost, therefore, adsorption is a favorable choice for heavy metal removal because it had simple, low cost, environmental friendly and no sludge generation [7]. Different types of adsorbents have been used for the removal of nickel metal ion and a variety of pollutants from water. Many researchers have made their efforts for developing inexpensive, available and environmentally friendly adsorbents based on agricultural and industrial wastes by-products such as peat [8], rice hull ash [9], hydrous titanium oxide [10], fly ash [11], sawdust [12], coconut shell [13], sugarcane bagasse [14], red mud [15], all these adsorbents show many disadvantages because of their tight pore size, wide pore size distribution, heterogeneous pore structure, low selectivity and capacity due to their weak interactions with metallic ions, their difficult and very expensive reactivation process, and they need more chemical treatment before use [16]. Recently, nanoparticles have received significant attention due to their novel properties and have come up as an area of extensive research in their utilization as adsorbents [6]. Where, nano materials are looked as most appealing materials because of their possibility applications especially for natural difficulties, for example, in treatment of waste water [7]. Through literature survey, there were found more examinations have been tended to use nanoparticles as active and powerful adsorbents for expulsion of heavy metals from water framework. Among the accessible adsorbents, nanoparticles composite from metal ion oxides, for example,  $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Cs}_2\text{O}$  [17],  $\text{CuO}$ ,  $\text{ZnO}$  and graphene oxide (GO) that are named the promising and alluring sorption materials for harmful metals expulsion from water frameworks because of their high amplitude and proficiency to expel these metals to meet the severe guidelines [18]. In addition, nanoparticles can enter into the pollution zone while other particles cannot such as micro particles [19]. Although adsorption studies of heavy metal ions on metal oxide nanoparticles have been reported before, relatively few studies have been investigated on the removal of Ni(II) ions by ZnO nanoparticles [8]. The aim of this paper is to checking up the ZnO nanoparticles ability as adsorbent to remove Ni(II) heavy metal ion from synthetic wastewater in a batch system and investigating the effect of temperature on the Ni(II) adsorption process for determining the thermodynamic properties. In addition the equilibrium adsorption isotherms and the adsorption kinetics for Ni(II) solution were studied.

## 2. Experimental Work

### I. Materials

In this paper, all the chemical substances were utilized with no other refinement. The specification of the used materials is presented in Table 1.

**Table 1: Properties of materials used in this study**

Material	Chemical formula	Purity (wt. %)	Origin
Zinc oxide	ZnO	98.0	China
Nickel sulfate	NiSO <sub>4</sub>	98.5	Sigma-Aldrich Germany
Sodium hydroxide	NaOH	99	BDH England
Hydrochloric acid	HCl	36	Thomas Baker Mumbai- India

## II. Characterization of ZnO nanoparticles

ZnO powder material was characterized using the X-ray diffraction device (XRD-6000, Shemadue) in the diffraction angle range  $20^\circ \leq 2\theta \leq 80^\circ$ , with monochromatic Cu K radiation ( $\lambda = 1.5406 \text{ \AA}$ ) source. The X-ray source emits radiation at (0.15405 nm) wavelength. The structural analysis was identified by scanning electron microscopy SEM (Te-scan VEGA 3 SB). The compositions of ZnO nanoparticles material was determined by energy dispersive X-ray spectroscopy (EDS). To analyze the chemical bonds and the functional groups grafted on to the ZnO nanoparticles material, FTIR measurements (Bruker –Tensor 27/ Germany) was used. The specific surface area of the ZnO was measured using instrument model Q-surf 9600 (USA), based on Brunauer, Emmett and Teller (BET).

## III. Preparation of adsorbate solution

Nickel sulfate stock solution (300 mg/L) was prepared by dissolving 0.791 g of NiSO<sub>4</sub> in 1000 ml distilled water. For further experiments, the stock solution of Ni(II) was diluted to obtain working solutions of varying concentrations, i.e. (40 to 300 mg/L). 0.1M NaOH and 0.1M HCl were used for the adjustment of the pH ranges from (2 to 6). The concentrations of metal ion after adsorption were measured by UV spectrophotometer [Type: SHIMADZU AA-7000, origin: Japan].

## IV. Batch nickel adsorption

Batch experiments were performed to evaluate the parameters that influence the process of adsorption of Ni (II) ions on ZnO nanoparticles. In this method, adsorption of Ni(II) was studied using aqueous solutions of nickel sulfate at different temperatures by taking 250ml flask containing 50ml metal solution of known concentration and pH; where pH of the solution was adjusted using dilute HCl or NaOH as per requirement. After adsorbent addition the mixture was stirred by magnetic stirrer at 240 rpm for interval of time then the adsorbent was separated by filtration using filter paper [Type: Whatman 542, origin: England] and the final liquids were analyzed for estimated the final residual concentrations of Ni(II) ions at a maximum wavelength of 393 nm using UV-visible spectrophotometer [Type: U.V-1100, Origin: China]. Table 2 shows the range of variables which were studied.

**Table 2: Range of parameters that were studied**

Variables	Operating range	Unit
pH	2 - 6	-
Contact time	10-50	min
ZnO dose	0.05 - 0.25	g
Ni(II) Initial concentration	40 - 300	mg/L
Temperature	25 - 40	C°

The percentage removal was calculated according to eq. (1) [18]:

$$\% \text{ Removal} = \left[ \frac{C_o - C_f}{C_o} \right] * 100 \quad (1)$$

where  $C_o$  and  $C_f$  are the initial and final concentrations of nickel metal ion in the aqueous solution (mg/l). The amount of Ni (II) ions in the filtered solution was estimated according to eq. (2) [20]:

$$q_e = \left[ \frac{C_o - C_e}{M} \right] * V \quad (2)$$

Where:  $q_e$  is the amount of Ni (II) adsorbed at equilibrium in (mg/g),  $M$  is the adsorbent mass in (g), and  $V$  is the volume of solution in (L).

### 3. Mathematical Concepts

#### I. Adsorption equilibrium modeling

The data of adsorption have been applied to Langmuir and Freundlich isotherms which are the widespread models depicting the solid-liquid adsorption process. Isotherms are the equilibrium relations between the concentration of adsorbate on the solid phase and its concentration in the liquid phase and from these isotherms the maximum adsorption capacity can be obtained.

##### 1) Langmuir-isotherm model

The Langmuir isotherm model assumes that the uptake of metal ions occurs on a homogeneous surface by a monolayer adsorption without any interaction between adsorbed ions. The linearized form of this isotherm can be expressed as [21]:

$$\frac{C_e}{q_e} = \frac{1}{K_1 q_m} + \frac{C_e}{q_m} \quad (3)$$

Where,  $q_e$  is the equilibrium loading of metallic ion over the solid particles (mg/g),  $C_e$  is the equilibrium loading of ion in the liquid (mg/L),  $q_m$  is the monolayer biosorption ability of the solid (mg/g), and  $K_1$  is the Langmuir constant linked to the adsorption free energy.

Moreover, a dimensionless equilibrium parameter  $R_L$  shows the isotherm is favorable, unfavorable, irreversible, or linear when the value of ( $R_L < 1$ ), ( $R_L > 1$ ), ( $R_L = 0$ ) and ( $R_L = 1$ ) respectively. It is expressed by equation [22]:

$$R_L = \frac{1}{1 + K_1 \cdot C_0} \quad (4)$$

Where,  $K_1$  is constant of Langmuir in (L/mg) and  $C_0$  is the initial nickel concentration in (mg/L).

##### 2) Freundlich isotherm model

The Freundlich isotherm model describes the multilayer sorption and it is expressed by the following equation [23]:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (5)$$

Where,  $K_f$  is constant of Freundlich in (mg/g) identified with the adsorption limit of zinc oxide nanoparticles and  $n$  is the adsorption intensity in (L/g).  $n^{-1}$  evaluates the degree of heterogeneity for surface sites [24].

#### II. Adsorption Kinetic models

A study of kinetics of adsorption is desirable as it provides information about the mechanism of adsorption. The kinetics of Ni(II) adsorption onto ZnO nanoparticles was evaluated using different models such as pseudo-first-order and pseudo-second order.

##### 1) Pseudo-first-order model

The pseudo-first-order rate by Lagergren has widely been used. The linearized adsorption rate expression is as follows [25]:

$$\log(q_e - q_t) = \log q_e - \left(\frac{K_1}{2.303}\right) t \quad (6)$$

Where,  $q_e$ : equilibrium capacity for metallic ions adsorbed per unit mass of the solid (mg g<sup>-1</sup>),  $q_t$ : metallic ions adsorbed per unit mass of the solid (mg g<sup>-1</sup>) at time  $t$ , and  $K_1$ : rate constant of first order adsorption in (min<sup>-1</sup>).

##### 2) Pseudo-second-order model

Pseudo-second-order rate model can be represented in the following form [26]:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

Where,  $q_e$ : equilibrium capacity for metallic ions adsorbed per unit mass of the solid (mg g<sup>-1</sup>),  $q_t$ : metallic ions adsorbed per unit mass of the solid (mg g<sup>-1</sup>) at time  $t$  and  $K_2$ : rate constant of 2<sup>nd</sup> order adsorption in (gmg<sup>-1</sup> min<sup>-1</sup>).

#### III. Adsorption Thermodynamics

The determination of thermodynamic parameters has a great importance to evaluate spontaneity and heat change for the adsorption reaction.

The free energy changes ( $\Delta G^\circ$ ) for the adsorption equilibrium is calculated from the distribution coefficients:

$$\Delta G^{\circ} = -R \cdot T \cdot \ln K_C \quad (8)$$

To check the impact of temperature on the procedure, the evacuation of Ni (II) particles from their blend by nanoparticles adsorbent was analyzed in the range 298–313 K. The dispersion coefficient ( $K_C$ ) was determined as:

$$K_C = \frac{q_e}{C_e} \quad (9)$$

Where  $q_e$  is the amount of nickel ion adsorbed at equilibrium in (mg/g) while,  $C_e$  is the equilibrium concentration in (mg/ L).

And through the Gibbs–Helmholtz equation the  $\Delta G^{\circ}$  free energy changes was related to the  $\Delta H^{\circ}$  enthalpy change and  $\Delta S^{\circ}$  entropy change as:

$$\Delta G^{\circ} = \Delta H^{\circ} - T \cdot \Delta S^{\circ} \quad (10)$$

It is possible to determine  $\Delta G^{\circ}$ ,  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  using the slope and intercept of Van't Hoff scheme of  $\ln K_C$  versus (1/T) through Eq.11 [20]:

$$\ln K_C = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \quad (11)$$

Where R is the universal gas constant equal (8.314 J/mol K) and T is the temperature (K).

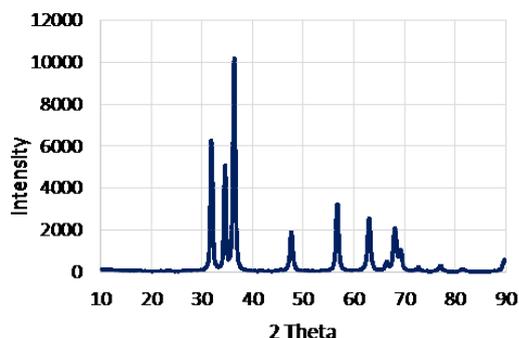


Figure 1: Pure zinc oxide nanoparticles -XRD analysis

## 4. Results and Discussion

### I. Adsorbent identification

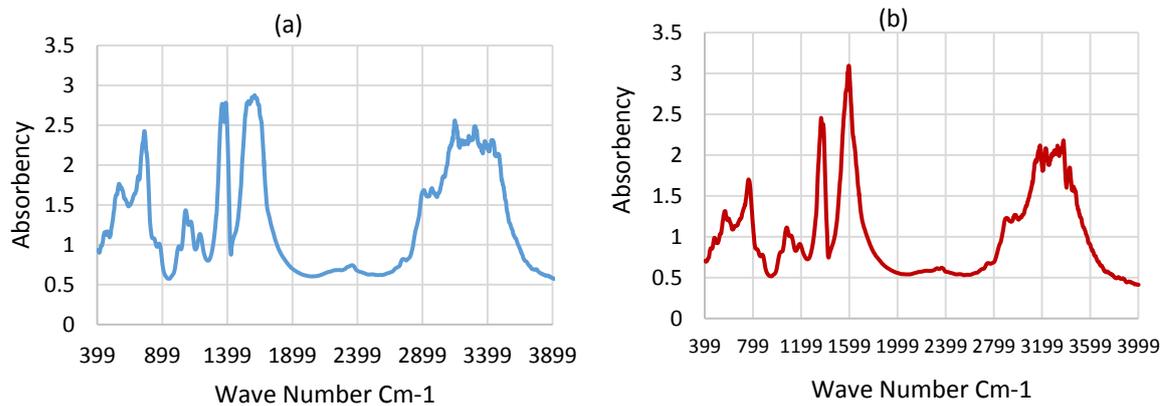
#### a) X-Ray diffract test

XRD image of pure ZnO nanoparticles is shown in Figure 1. The nanoparticle construction, structural character, and phase structure were analyzed by (XRD) with  $2\Theta$  range from  $10^{\circ}$  to  $90^{\circ}$  with scan rate 2 (deg/min) and Cu- $\alpha$  ( $\lambda = 1.541$ ) as radiation source was applied.

The peaks were seen at 31.73, 34.39, 36.24, 47.51, 56.52, 62.88, 67.94, 72.54, 76.89 and 81.98, that can be referred to detect the nanoparticles which are of pure zinc oxide with a hexagonal structure. These results are in a good agreement with the result of [25].

#### b) FTIR spectra test

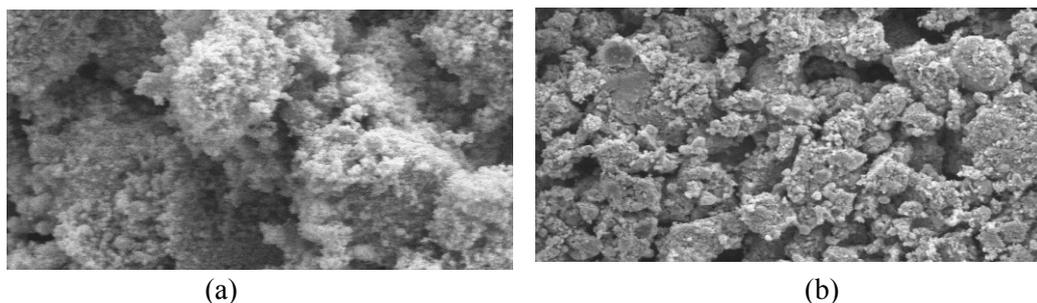
Fourier-transform infrared spectroscopy (FT-IR) spectra for the adsorbent zinc oxide nanoparticles in two state; pure and Ni (II) loaded ZnO nanoparticles are shown in Figure 2. A number of absorption peaks of unloaded adsorbent can be assigned in Figure 2a which shows clear and enlarged FTIR spectrum. The bands observed between  $(3240.41-3377.36) \text{ cm}^{-1}$  are assigned to asymmetric -OH present to alcohol groups and the peak  $1658.78 \text{ cm}^{-1}$  is assigned to alkene C=C stretching. The peak at  $1381.03 \text{ cm}^{-1}$  may represent alkane C-H bending while the peak at  $1078.21 \text{ cm}^{-1}$  is due to C-O stretching in alcohol. Also, a wide absorption band around  $428-570 \text{ cm}^{-1}$  is referred to the mineral zinc-oxide extension group. The results of FT-IR spectra for zinc oxide nanoparticles are in a good agreement with study [20]. Figure 2b depicts the FT-IR spectra after Ni(II) filled, the wide peak at  $3429.43 \text{ cm}^{-1}$  which is related to O-H stretching that present in alcohol and climbs during adsorption method. The intensity of the peak at  $1658.78 \text{ cm}^{-1}$  is considerably diminished to  $1597.06 \text{ cm}^{-1}$  after Ni (II) loaded. The move of the peak from  $1078.21$  to  $1080.14 \text{ cm}^{-1}$  suggests the contribution of the C-O set in limited Ni (II). These results are in agreement with a previous reported study [27].



**Figure 2: (a) Fourier-transform infrared spectroscopy test for a pure zinc oxide nanoparticles, (b) Ni (II) - accumulated on zinc oxide nanoparticles.**

c) Surface morphology test

SEM measurement of the able to adsorb substances is the most significant estimation since the adsorption limit principally relies upon structure and porosity for the surface [20, 27]. Figure 3 shows the SEM images of ZnO nanoparticle. From Figure 3a, represents pure ZnO nanoparticles. After Ni (II) loaded (Figure 3b), the nanoparticles are fully covered with the metal. It can be observed that the surface morphologies of ZnO are different before and after Ni (II) loaded.



**Figure 3: SEM tests of a) pure zinc oxide nanoparticles, b) Ni (II)-loaded ZnO nanoparticles.**

d) BET analysis

The Brunauer–Emmett–Teller BET analysis technique was applied for the measurement of the specific surface area of materials. The surface area of ZnO sample was measured equal to 29.68 m<sup>2</sup>/g.

e) Elemental test

The elemental surface composition of the ZnO was determined from the energy dispersive spectroscopy EDS which is shown in Figure 4 (a and b). The presence of Zn and O without any impurity element was confirmed from the Fig. 4a. The pattern shows that the composition of ZnO sample has a Zn - 84.9 % and O - 15.1 %. Fig. 4b shows the EDS spectra of Ni doped ZnO sample. The EDS spectrum indicates that the synthesized Ni doped ZnO sample mainly contains Zn, Ni, and O elements with a composition of Zn – 76.4 %, O - 20.4 % and Ni - 3.2 %. The EDS spectral peaks of O appeared at 0.5 keV; Zn appeared at 1, 8.4, and 9.6 keV; while Ni appeared at 1.5keV respectively.

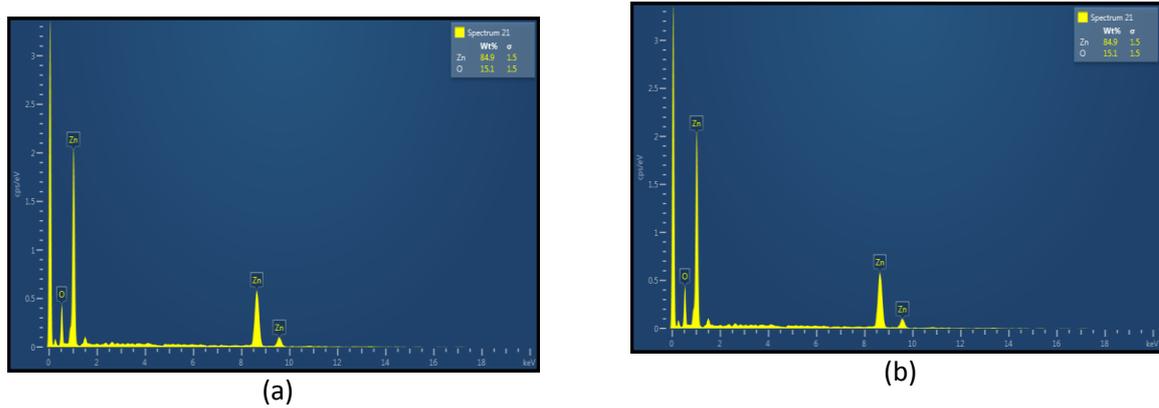


Figure 4 : Energy dispersive X-ray Spectroscopy of (a) Pure ZnO and (b) Ni+2doped ZnO Nanoparticles

## II. Adsorption studies

### a) Effect of pH

The most important factor that affecting the metals adsorption processes on the adsorbent is the pH level of the solution, since the pH indeed has an influence on surface chemistry and on surface charge. Thus the pH of the aqueous solution affects the solubility of the metal ions, concentration of the counter ions on the functional groups on the sorbent and the ionization grade of the sorbent throughout the reaction [28]. The influence of pH on uptake efficacy for Ni (II) ion at ZnO nanoparticles was studied within the range (2-6) at room temperature, and the results obtained are presented in Figure 5. It was observed that the removal efficiency for the metal increases sharply as the solution pH increased. At lower pH (less than 4), the surface would become more positively charged leading to strong repulsive forces which inhibit the approach of positively charged nickel cation to the binding sites, and as a result of that the interaction between metals ions and adsorbent surface would decrease. When the pH of solution increased from 4 to 5 a slight increase in removal efficiency, moreover, as the pH of the solution increases up to 5 the repulsion between the surface and metals cations decreases leading to increasing the removal efficiency up to maximum removal efficiency reached 98.71% for Ni(II) at pH 5. But higher pH more than 5 (at pH 6) decrease in removal efficiency was observed as precipitation of metal ions occurs as its hydroxides would be formed. It is found the best value of pH for the removal of Ni(II) ions from aqueous solution at which neither precipitation of the metal hydroxide occurs at pH 5 as studied by [29,30].

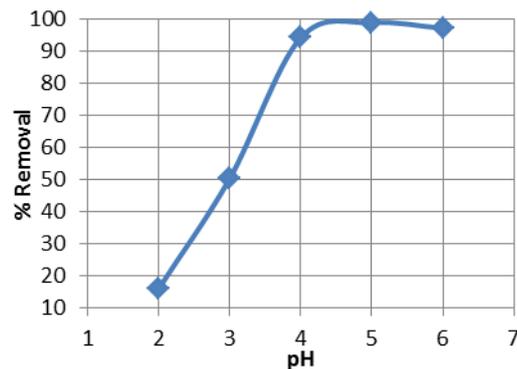
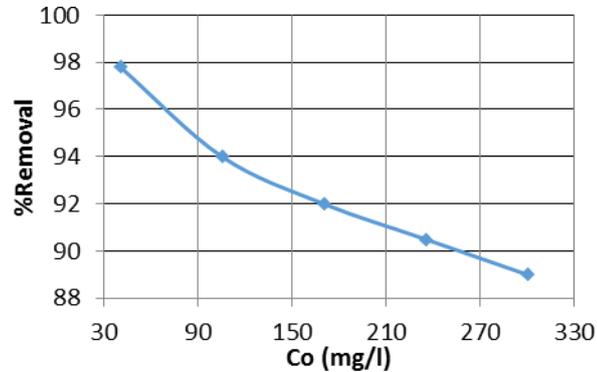


Figure 5: Effect of solution pH on percentage removal efficiency at initial concentration 300 mg/L, time 30min and amount of adsorbent 150mg

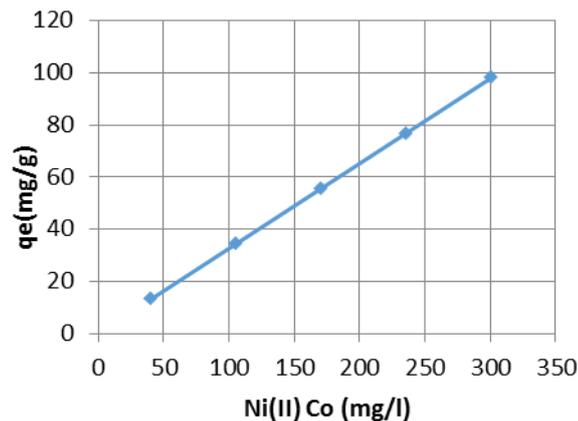
### b) Effect of initial Ni (II) concentration

The removal of Ni (II) from the synthetic waste water was done at primary concentrations extending from (40 to 300) mg/L. Figure 6 demonstrates that when expanding initial nickel concentration the level of expulsion of metal reduces too. This abatement was a result for the minimal number of effective locations to zinc oxide nanoparticles that become filled with nickel particles when its concentration rising [2,13]. For Ni (II) ion there is a gradually drop in percentage removal at higher initial concentration. While in Figure 7, the results shown the amount of Ni (II) ions per unit of ZnO nanoparticles were increased with increasing the initial Ni (II) loading in the working range. The

enhancement in adsorption is an outcome of the rise in concentration difference improved between the bulk of liquid and solid surface [31]. At greater loadings of Ni (II) ions, the driving force is higher and as the energetic sites of ZnO surface were enclitic by a greater number of metallic ions, the adsorption persists resulting an enhanced capture of metallic ions from liquid [25,32]. Thence, the maximum adsorption capacity took place when the initial metal ion concentration was maximum i.e. 300 mg/l. These results agree well with the previous finding of other similar systems [2, 9, 13].



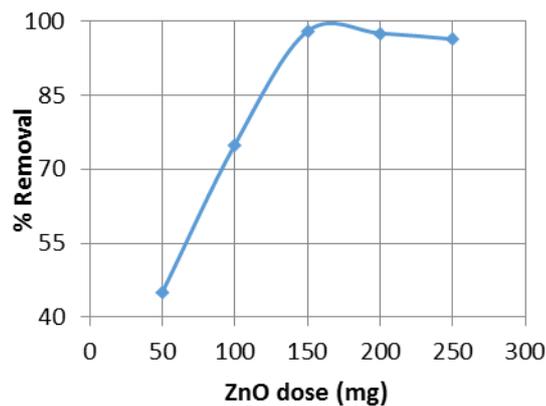
**Figure 6: Effect of initial Ni (II) concentration on the percentage removal ZnO nanoparticles, 50 ml solution, dosage 150mg, pH=5 and contact time 30 min.**



**Figure 7: adsorption capacity (qe) vs. Nickel ion initial concentration at pH=5, 50 ml solution, dosage 150mg and contact time 30 min.**

### c) Effect of adsorbent dose

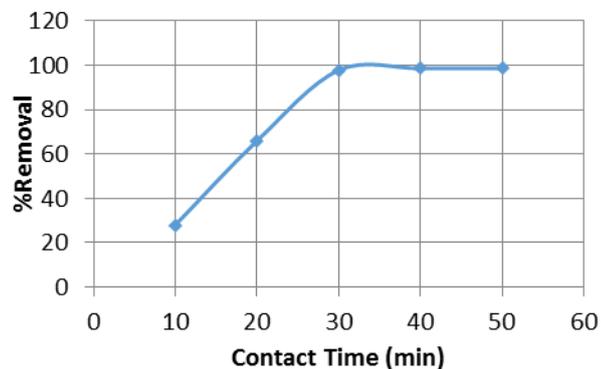
The effect of adsorbent dose (ZnO nanoparticles) on the percentage removal of Ni (II) ions from their aqueous solutions was examined by varying the amount of adsorbent from 0.05 to 0.25 gm per 50ml at pH 5 for a contact time of 30 min as shown in Figure 8. With increase in the amount of adsorbent, percentage removal of Ni (II) ions was found to increase too. The rapid increase in adsorption with the increase in adsorbent dose can be attributed to increased availability of binding sites resulting from the increased dose and conglomeration of the adsorbent [33]. It was observed that Ni (II) removal efficiency increased with increasing adsorbent dose, up to 150 mg after which it became almost constant. After the critical dose, the extent of adsorption slows down due to the fact that although there is increasing number of binding sites but decreasing the number of ions remaining in the solution; these results show the same trend as obtained by [34,35].



**Figure 8: Effect amount of adsorbent on percent removal of Ni(II), initial concentration 300 mg/l, time 30 min, pH=5.**

d) Effect of contact time

The relationship between contact time and the percentage removal of Nickel ion by ZnO nanoparticles is shown in Figure 9. The effect of contact time was studied at room temperature and the percentage removal was found to increase with increasing the contact time reach an equilibrium adsorption is established at maximum value after 30 min. At the beginning there is rapid increase in the removal efficiency; this is due to the large number of vacant surface sites available for adsorption. After that, the percent removal efficiency becomes unchanged by further increase in contact time; because the number of available adsorption sites saturated with amount of Ni (II) adsorbed on zinc oxide and no significant increase in removal efficiency will occurred, and then the equilibrium will be established [8,36].



**Figure 9: Effect of contact time on percent removal of Ni(II), initial concentration 300 mg/l, dosage 0.15 g. and pH=5**

e) Temperature influence

The influence of temperature on Ni(II) uptake, with keeping Ni loading and pH unchanged at 300 mg/L and 5 respectively, is shown in Figure 10. It is observed in this figure, that the percent removal of Ni (II) ions, over the ZnO surface, increased slightly with increasing temperature. This behavior of the removal with a rising in temperature revealed that higher temperature boosts the uptake of Ni (II) ions by ZnO. This effect proposed an exegesis of the adsorption pathway linked to the uptake of Ni (II) ions over ZnO in which the adsorption emerges from the electrostatic interaction interconnected with little heat of adsorption [37]. This denotes that the adsorption operation has an endothermic behavior. These results are consistent with the other studies [2, 9].

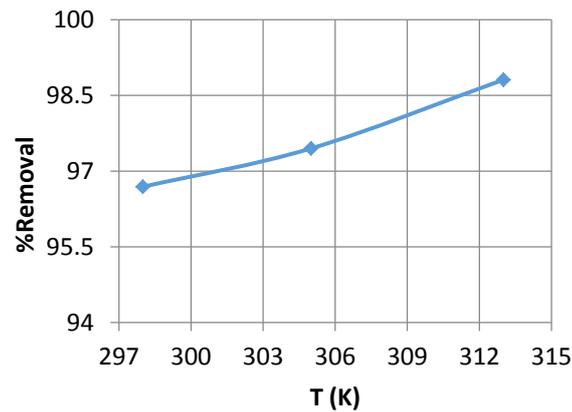


Figure 10: Effect of temperature on percent removal of Ni(II), initial concentration 300 mg/l, dosage 0.15 g. and pH=5.

### III. Equilibrium models

#### a) Langmuir-isotherm

Adsorption isotherms of Ni(II) ions on ZnO nanoparticles were persistent at different initial concentrations, time 30min, pH=5, 50 ml aqueous, dosage 150mg and temperature 25 °C. The values of  $1/q_m$  and  $(1/k_1 \cdot q_m)$  are determined by the incline of the straight plots of  $C_e/q_e$  versus  $C_e$  (Figure 11). The data explained in Table 3 demonstrate that  $R_L$  is greater than 0 but less than 1, indicating that the Langmuir isotherm of nickel ion on zinc oxide nanoparticles is a favorable method.

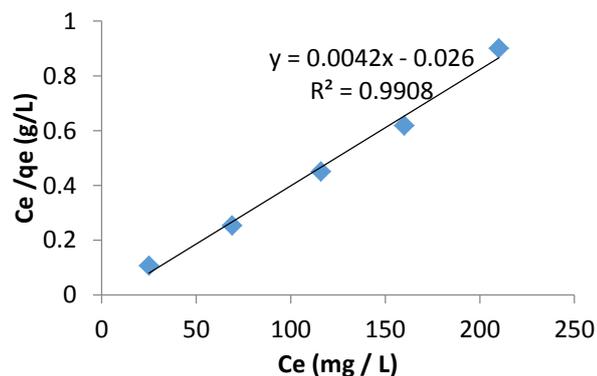


Figure 11: Langmuir Isotherm for adsorption of Ni (II) on ZnO nanoparticles at different initial concentrations, time 30min, pH=5, 50 ml aqueous, dosage 150mg and temperature 25 °C.

#### b) Freundlich isotherm

The Freundlich isotherm parameters for adsorption of Ni (II) on ZnO were obtained by fitting the experimental data for different initial concentrations and at constant temperature 25 °C. The relationship between  $\ln(q_e)$  and  $\ln(C_e)$  can be seen in Figure 12, through which we can find values of the Freundlich constant ( $K_f$ ) and adsorption intensity ( $n$ ). The data listed in Table 3 show that  $n$  are  $> 1$ , indicating that the adsorption procedure is favored. It can be seen from Table 3 that the experimental data follow the Langmuir isotherm model better than the Freundlich isotherm model and  $R^2=0.990$ .

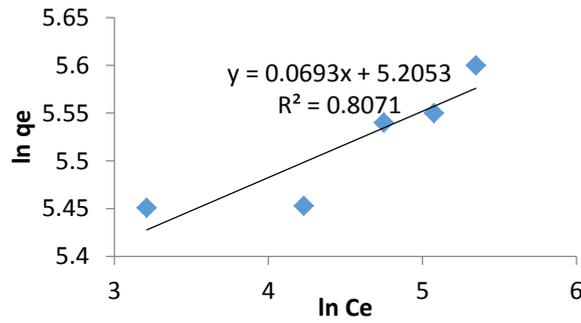


Figure 12: Freundlich model for Ni (II) adsorption on ZnO nanoparticles at different initial concentrations, time 30min, pH=5, 50 ml aqueous, dosage 150mg and temperature 25 °C

Table 3: Parameters of isotherm models

Langmuir				Freundlich		
q <sub>m</sub>	R <sub>L</sub>	K <sub>1</sub>	R <sup>2</sup>	K <sub>f</sub>	n	R <sup>2</sup>
250	0.0211	0.154	0.990	182.181	14.493	0.807

IV. Kinetic models

a) Pseudo-first-order

Using the pseudo-first-order model to fit the kinetic data as shown in Figure 13, the values of K<sub>1</sub>, q<sub>e</sub> and correlation coefficient R<sup>2</sup> have been calculated from the slope and the intercept of the linear plot of log (q<sub>e</sub> - q<sub>t</sub>) versus t which came out to be 0.1543min<sup>-1</sup>, 147.299 mg/g and 0.933 respectively. The adsorption of Ni (II) ions on ZnO nanoparticles kinetic model was conducted at conditions of initial metal nickel ion concentration 300 mg/L, solution pH 5, 50 ml aqueous, dosage 150mg and temperature 25 °C.

b) Pseudo-second-order

Using a pseudo second-order model to fit Ni (II) ions sorption onto ZnO nanoparticles, the form of t/q<sub>t</sub> against t is a straight line as shown in Figure 14. The q<sub>e</sub> and K<sub>2</sub> values determined from the slope and intercept of the plot respectively, where the value of q<sub>e</sub> is 29.762 mg/g and K<sub>2</sub> 0.0122(g/mg. min). The correlation coefficient for the second-order kinetics model is 0.998, indicating the applicability of this kinetic equation and the second-order nature of adsorption process of Ni(II)ions onto ZnO nanoparticles.

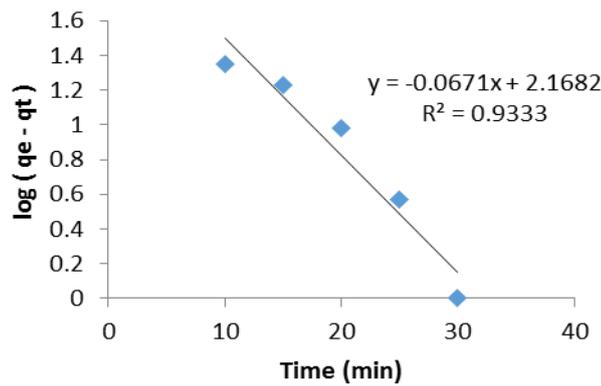


Figure 13: Pseudo first order kinetic plot for Ni (II) adsorption

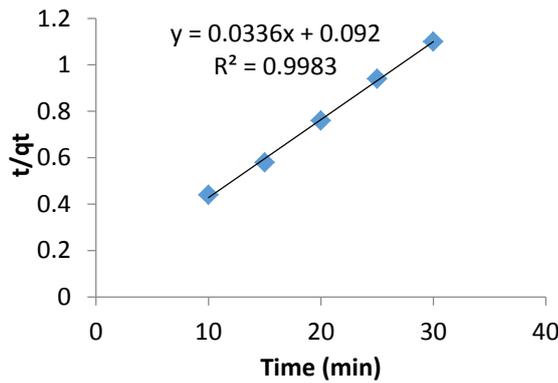


Figure 14: Pseudo second order kinetic plot for Ni (II) adsorption

The correlation coefficient of the second order kinetic model (0.998) was higher than the first-order kinetic model (0.933), therefore, the Pseudo second order model is well depicting the uptake of Ni (II) over ZnO nanoparticles. The pseudo second order model is established on the assumption that the step which determining rate of adsorption may be chemical adsorption which contains participation forces for electrons of the adsorbate and adsorbents [30].

V. Thermodynamics models

The parameters of thermodynamics  $\Delta H^\circ$ ,  $\Delta G^\circ$  and  $\Delta S^\circ$  for the adsorption process of Ni<sup>+2</sup> on ZnO obtained from the slope and intercept for the scheme of  $\ln K_c$  as a function of  $1/T$ . The plot yields a straight line as shown in Figure 15, and the results of thermodynamic parameters presented in Table 4.

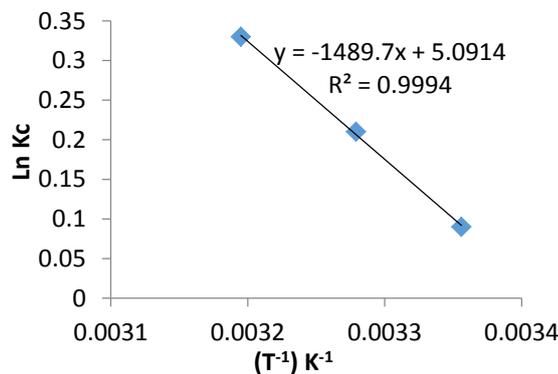


Figure 15:  $\ln K_c$  against  $1/T$  for sorption of Ni<sup>+2</sup> ions at incipient loading of Ni<sup>+2</sup>(300 mgL<sup>-1</sup>) and ZnO loading (0.15 g)

Table 4: Parameters of thermodynamics for the sorption of Ni<sup>+2</sup> over ZnO

Temp. K	$\Delta H^\circ$ (kJ/mol)	$\Delta G^\circ$ (J/mol)	$\Delta S^\circ$ (J/mol.K)
298	12.379	-0.235	42.33
305		-0.532	
313		-0.871	

$\Delta G^\circ$  must always be negative for a method to be thermodynamically pleasant [37]. The negative values of  $\Delta G^\circ$  for the employed temperatures are connotative of the degree of spontaneous nature of the sorption method. It is observed that as temperature raised from 298 to 313,  $\Delta G^\circ$  decreased from -0.235 to -0.871 enhancing the spontaneous behavior of the process which favored the adsorption of nickel ions at higher temperature.

The positive value of  $\Delta H^\circ$  (12.379 kJ/mol) proposed an endothermic behavior of the adsorption mechanism. This is compatible with the rising Ni (II) removal with temperature as seen in Fig. 10. Also the  $\Delta H^\circ$  value acquired, in the present work, is less than 40 kJ/mol suggesting the physical

adsorption process. When physical sorption is described by enthalpy changes that are small in the range of ( 10- 40 )kJ/ mol, while the chemisorption range of (40-400) kJ/mol [38].

As observed in Table 4,  $\Delta S^0$  has a positive amount indicating an increase in the stochastic process at the solid-liquid interface throughout the sorption course [2, 6].

## 5. Conclusion

The influence of different process variables like residence time, liquid pH, incipient loadings, temperature, and ZnO loadings were studied for the uptake of Nickel ions from aqueous mixture by ZnO nanoparticles. The highest removal of Nickel ions was obtained at 0.15 g of ZnO, 30 min, 5 PH and 300 ppm respectively. Furthermore, results obtained approved that the temperature affected on the efficiency of the process. The isotherm study has indicated that Langmuir model provided a better fit for the experimental data of Ni (II) adsorption onto zinc oxide, while the adsorption kinetics demonstrated that; the adsorption mechanism followed the pseudo second-order. The thermodynamic study has confirmed that the adsorption process is endothermic and spontaneous, due to the negative values estimated for  $\Delta G^0$ . The present work confirmed the ability of ZnO nanoparticles for the removal of Nickel ions from aqueous mixture with high efficiency in small amounts and low cost.

## Acknowledgment

The author gratefully acknowledges Center of the Nanotechnology Advanced Material Research and Department of Chemical Engineering, University of Technology, Baghdad, Iraq for supporting this research.

## References

- [1] K. Nalwa, A. Thakur , N. Sharma, "Synthesis of ZnO nanoparticles and its application in adsorption," *Advanced Materials Proceedings*, 2, 11, 697-703, 2017.
- [2] A.M. Ahmed, A. E. Ali , A. H. Ghazy, "Adsorption separation of nickel from wastewater by using olive stones," *Advanced Journal of Chemistry-Section A*, 2, 1, 79-93, 2019.
- [3] WHO, "Guidelines for drinking-water quality," fourth edition, 2012.
- [4] Iraqi regulation, "Environmental legislation," Chapter XI", 2001.
- [5] A. Baysal, N. Ozbek , S. Akman, "Determination of trace metals in waste water and their removal processes," *Waste Water - Treatment Technologies and Recent Analytical Developments*. Ch.7, 2013.
- [6] M. K. Moftakhar, M. R. Yaftian, M. Ghorbanloo, "Adsorption efficiency, thermodynamics and kinetics of Schiff base-modified nanoparticles for removal of heavy metals," *Int. J. Environ. Sci. Technol.*13:1707–1722, 2016.
- [7] A. A. Alswata, M. B. Ahmad , N. M. Al-Hada, "Preparation of zeolite/zinc oxide nano composites for toxic metals removal from water," *Results in Physics*, 7,723–731, 2017.
- [8] P. Bartczak, M. Norman, M. Wysokowski, J. Zdarta, F. Ciesielczyk, T. Jesionowski, "Removal of nickel (II) and lead (II) ions from aqueous solution using peat as a low-cost adsorbent: A kinetic and equilibrium study," *Arabian Journal of Chemistry*, 11, 1209–1222, 2018.
- [9] C.I. Lin, L.H. Wang, "Adsorption of nickel (ii) ion from aqueous solution using rice hull ash," *Journal of chemical engineering of Japan*, 29, 2011.
- [10] K. Atkovska, K. Lisichkov, G. Ruseska, A. T. Dimitrov, A. Grozdanov, "Removal of heavy metal ions from wastewater using conventional and nanosorbents: a review," *Journal of Chemical Technology and Metallurgy*, 53, 2, 202-219, 2018.
- [11] A. Ashfaq, A. Ali, R. Goel, S. Ram, "Removal of nickel ions from aqueous solutions using fly ash: equilibrium and kinetic studies," *International Journal of Advance Research in Science and engineering*, 6, 5, 2017.
- [12] L. F. Muhaisen, "Nickel ions removal from aqueous solutions using sawdust as adsorbent: equilibrium, kinetic and thermodynamic studies," *Journal of Engineering and Sustainable Development*, 21, 03, 2017.
- [13] B. Olufemi1, O. Eniodunmo1, "Adsorption of nickel(II) ions from aqueous solution using banana peel and coconut shell," *International Journal of Technology*, 9, 3, 434, 2018.

- [14] I. Aloma, M.A. Martin-Lara, I.L. Rodriguez, G. Bla'zquez, M. Calero, "Removal of nickel (II) ions from aqueous solutions by biosorption on sugarcane bagasse," *Journal of the Taiwan Institute of Chemical Engineers*, 43, 275–281, 2012.
- [15] A. I. Zouboulis, K. A. Kydros, "Use of red mud for toxic metals removal: the case of nickel," *J. Chem. Tech. Biotechnol*, 58, 95-101, 1993.
- [16] Z. Hejri, M. Hejri, M. Omidvar, S. Morshedi, "Synthesis of TiO<sub>2</sub>/nZVI nanocomposite for nitrate removal from aqueous solution," *International Journal of Industrial Chemistry*, 21,1,2019.
- [17] S. Mahdavi , M. Jalali, A. Afkhami, "Heavy metals removal from aqueous solutions by Al<sub>2</sub>O<sub>3</sub>nanoparticles modified with natural and chemical modifiers," *Clean Techn Environ Policy*, 17,85–102, 2015.
- [18] S. Mahdavi , M. Jalali, A. Afkhami, "Removal of heavy metals from aqueous solutions using Fe<sub>3</sub>O<sub>4</sub>, ZnO, and CuO nanoparticles," *J Nano part Res.*, 14,846, 2012.
- [19] E. A. Deliyanni, G. Z. Kyzas, K. S. Triantafyllidis, K. A. Matis, "Activated carbons for the removal of heavy metal ions : A systematic review of recent literature focused on lead and arsenic ions," *Open Chem.*, 13, 699–708, 2015.
- [20] G. Yuvaraja, C. Prasad, Y. Vijaya, M. V. Subbaiah, "Application of ZnO nanorods as an adsorbent material for the removal of As (III) from aqueous solution: kinetics, isotherms and thermodynamic studies," *International Journal of Industrial Chemistry*, 9, 17–25, 2018.
- [21] S. Singh, L. K. Verma, S. S. Sambhi, S. K. Sharma," Adsorption behavior of Ni(II) from water onto zeolite X: kinetics and equilibrium studies," *Proceedings of the World Congress on Engineering and Computer Science* , October 22 - 24, San Francisco, USA, 2008.
- [22] S. Erol , M. Ozdemir, "Kinetics, equilibrium and thermodynamics studies on Cd(II) removal from aqueous solution by magnesite tailing," *Indian Journal of Chemical Technology*, 25, 246-254, 2018.
- [23] L. M. Cozmuta, A. M. Cozmuta, A. Peter, C. Nicula, E. B. Nsimba, H. Tutu, "The influence of pH on the adsorption of lead by Na-clinoptilolite: Kinetic and equilibrium studies," *Water SA*, 38, 2, 2012.
- [24] A. A. Alswata, M. B. Ahmad, N. M. Al-Hada, H. M. Kamari, M. Z. Hussein, N. A. Ibrahim, "Preparation of zeolite/zinc oxide nanocomposites for toxic metals removal from water," *Results in Physics*, 7 723–731, , 2017.
- [25] K. Nalwa, A. Thakur, N. Sharma, "Synthesis of ZnO nanoparticles and its application in adsorption," *Advanced Materials Proceedings*, 2, 11, 697-703, 2017.
- [26] M. Malakootian, N. Yousefi, A.Fatehizadeh, S. W. Van Ginkel, M. Ghorbani, S. Rahimi, M. Ahmadian, "Nickel (II) removal from industrial plating effluent by fenton process," *Environmental Engineering and Management Journal* ,14,4, 837-842, 2015.
- [27]R. Jeyachitra, N. Sriharan, V. Senthilnathan, T. S. Senthil, "Effect of Ni doping on structural, optical and photocatalytic properties of Zn1-X Ni X O nanoparticles prepared by different pH conditions," *Journal of Advances in Chemistry*, 12,6,2016.
- [28] D. Sud , G. Mahajan , M. P. Kaur, "Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions – a review," *Bioresource Technology*, 99, 6017–6027, 2008.
- [29] M. H. Ali, A. M. Abdel-Satar, "Removal of some heavy metals from aqueous solutions using natural wastes orange peel activated carbon," *IJRDO-Journal of Applied Science*, 3,3, 2017.
- [30]A. Heidaria, H. Younesi, Z. Mehraban, H. Heikkinen, "Selective adsorption of Pb(II), Cd(II), and Ni(II) ions from aqueous solution using chitosan–MAA nanoparticles," *International Journal of Biological Macromolecules*,9,22,2013.
- [31] R. B. Shaikh, B. Saifullah, F. U. Rehman, "Greener method for the removal of toxic metal ions from the wastewater by application of agricultural waste as an adsorbent," *Water*, 10, 10, 2018.
- [32] A. Çitak, "Synthesis, characterization, and kinetic studies of multi-functionalized mesoporous silica for adsorption of zinc," *Turkish Journal of Chemistry*, 43, 106 – 117, 2019.
- [33] K. M. Nguyen, B. Q. Nguyen, H. T. Nguyen, T.H. Nguyen, "Adsorption of arsenic and heavy metals from solutions by unmodified iron-ore sludge, *Applied Sciences*, 9, 619, 2019.
- [34] L. A. Ahmed, "Removal of heavy metals from waste water by date palm tree wastes," *Eng. &Tech. Journal*, 28, 1, 2010.
- [35] M. M. Brboot, B. A. Abid , N. M. Al-Shuwaiki, "Removal of heavy metals using chemicals precipitation," *Eng. & Tech. Journal*, 29, 3, 2011.

- [36] I. Kula, M. Ug̃urlu , H. Karaog̃lu, A. Celik, “Adsorption of Cd(II) ions from aqueous solutions using activated carbon prepared from olive stone by ZnCl<sub>2</sub>activation,” *Bioresource Technology*, 99, 492–501, 2008.
- [37] M. I. Khan, S. Akhtar, S. Zafar, A. Shaheen, M. A. Khan, R. Luque , A. Rehman, “Removal of congo red from aqueous solution by anion exchange membrane (ebtac): adsorption kinetics and thermodynamics,” *Materials*, 8, 4147-4161, 2015.
- [38] P. Saha, S. Chowdhury, “Insight into adsorption thermodynamics,” *Thermodynamics- chapter 16*, 349-367, Licensee Intech Open, 2011.