

Investigation of nickel adsorption onto low Jordanian zeolite dose: efficiency and Langmuir – Freundlich behaviour

Ziad Al-Ghazawi¹⁾, Ahmad Qasaimeh¹⁾ ✉, Bilal Al-Bataina²⁾

¹⁾ Department of Civil Engineering, Faculty of Engineering, Jordan University of Science and Technology, Irbid, 22110, 00962-2-7201000 22139; Jordan

²⁾ Department of Chemical and Biochemical Engineering, University of Western Ontario, Canada

RECEIVED 27.05.2020

REVIEWED 20.12.2020

ACCEPTED 15.01.2021

Abstract: In this work, nickel adsorption onto low Jordanian zeolite dose is being investigated. Natural zeolite doses were stirred continuously with nickel solutions in batch reactors at 180 RPM for 24 hours, where the temperature was set to 20°C. The pH was initially 4.5 and reached 5.2 at equilibrium. The removal efficiency of nickel reaches maximum value when the initial nickel concentration is around 1 ppm and then tends to decrease when the initial nickel concentration increases above 1 ppm. The optimal nickel removal reaches 65% when the initial nickel concentration is 1 ppm and the zeolite dose is 26 mg·dm⁻³. This study investigates the behaviour of nickel removal and modelling isotherms below and above this critical peak point. At this level of zeolite dose, the adsorption does not follow either Freundlich or Langmuir isotherms, but rather, it follows Freundlich for the data plot just below the peak point with the highest coefficient of determination (R^2) equals (0.98) when the zeolite dose is (26 mg·dm⁻³), whereas it follows Langmuir for the data plot just above the peak point with the highest coefficient of determination (R^2) equals (0.99) when the zeolite dose is (10 mg·dm⁻³). These findings clarify the theory behind each isotherm and can be used to find new information for efficient treatment techniques.

Keywords: batch reactor, Freundlich, isotherm, Langmuir, low dose, metals, nickel, wastewater, zeolite

INTRODUCTION

Heavy metal contamination of water is a crucial issue due to their toxicity to human and environments. Although heavy metals occur naturally, most of the environmental contaminations come from anthropogenic activities such as ore mining, industrial processes, and agricultural processes [TÓTH *et al.* 2016; VAREDA *et al.* 2019; VHAHANGWELE *et al.* 2018].

One of the heavy metals of concern is nickel as it exists in water supply networks, open water bodies, and groundwater. The primary source of nickel in tap-water is the leaching of nickel from pipes and fittings. Nickel may also be present in surface water from industrial effluents. In addition, nickel is present in groundwater as a consequence of its dissolution from nickel ore-bearing rocks [GONZALEZ *et al.* 2013; HEIKKINEN *et al.* 2002; VHAHANGWELE *et al.* 2018].

Adsorption is one of major processes used to separate metal pollutants as a simple technique for water and wastewater treatment. There are many efficient adsorbents that were widely used in water purification. In the literature, many adsorbent materials have been used such as activated carbon [POLLARD *et al.* 1992], clay materials [CRINI 2006; DE AGUIAR *et al.* 2002], biological masses [CRINI 2005], natural and artificial zeolites [BABEL *et al.* 2003; HEDSTROM 2001], and some other solids such as fly ashes and coagulants [WANG *et al.* 2006; 2008].

Zeolites are natural microporous aluminosilicate minerals that can be termed as a naturally available material with low stock cost and high resistance to alteration [MERCER *et al.* 1978]. Zeolite has a dimensional crystalline context of tetrahedral aluminosilicates/tectosilicate bonded together with replaceable cations. It is hydrated with water that fills the spaces in a volumetric style [KORKUNA *et al.* 2006; MUMPTON 1987].

Zeolite is widely used for the treatment of waters and reclaimed waters to remove pollutants such as metals, and ionized organic chemicals. The experimental procedure in the treatment methods can be set up either as fixed bed adsorption column [SHAFEEYAN 2014; XU *et al.* 2013] or as batch adsorption slurry reactor [GÜZEL *et al.* 2015; IMAGA *et al.* 2015; MITTAL *et al.* 2015].

Adsorption is characterized as a surface adhesion phenomenon. It occurs as a physical or chemical process depending on the adsorbent and adsorbate characteristics. The adsorption process in removing metals from industrial wastewater is assumed to be of a chemical type. In domestic wastewater treatment, the pollutants are organic matters. Hence, the adsorption is thought to be of a physical type [AL-JABARI 2016; 2017; AL-JABARI *et al.* 2012; 2015].

Adsorption process can be described mathematically in many ways; one of the formulations widely used is known as an isotherm. Isotherm describes the interaction between adsorbate and adsorbent, and their distribution relationship in an equilibrium condition. So as to examine the adsorption capability of an adsorbent in removing material in solution, the Freundlich and Langmuir isotherms are frequently utilized [FENG *et al.* 2009; WYCISZKIEWICZ *et al.* 2017; XIA *et al.* 2013; ZHANG *et al.* 2018].

The Freundlich isotherm was derived by Herbert Freundlich in 1909. It is the earliest known empirical relation describing the adsorption equilibrium between dissolved material and solid material. It represents the isothermal superficial adsorption for a dissolved material or a gas onto a solid material [HERZOG 1909]. It describes non-ideally reversible adsorption applied to multi-layer adsorption over a heterogeneous surface. One of the major disadvantages of the Freundlich equation is that it does not state an adsorption maximum limit [ADAMSON *et al.* 1967; FREUNDLICH 1906; SPARKS 2003].

Langmuir theory was developed originally for gas adsorption [LANGMUIR 1916]. Langmuir adsorption isotherm assumes monolayer adsorption that only occurs at a limited number of specific identical sites where there is no lateral interaction between the adsorbed molecules [VIJAYARAGHAVAN *et al.* 2016]. Langmuir isotherm refers to homogeneous adsorption as all sites retain equal affinity for the adsorbate [KUNDU *et al.* 2006]. It is characterized by saturation where an equilibrium point is reached and no further adsorption may take place [DEMIRBAS *et al.* 2008].

MATERIALS AND METHODS

ADSORPTION ISOTHERMS THEORY

In the adsorption process, the amount of substance adsorbed onto solid material as a function of substance concentration at a constant temperature will result in a function known as an adsorption isotherm. The adsorbed substance is called adsorbate, while the adsorbing material is called adsorbent. The amount that an adsorbent can take of an adsorbate depends on the concentration of adsorbate, the characteristics of adsorbate/adsorbent materials, and the temperature of the system. The amount of adsorbate can be estimated by using the following equation:

$$q_e = \frac{(C_o - C_e)V}{w} \quad (1)$$

where: q_e denotes for the equilibrium adsorption capacity of the adsorbent to uptake adsorbate ($\text{mg}\cdot\text{g}^{-1}$); C_o denotes for the initial adsorbate concentration ($\text{mg}\cdot\text{dm}^{-3}$), C_e denotes for the equilibrium adsorbate concentration ($\text{mg}\cdot\text{dm}^{-3}$), V denotes for the volume of the solution (L), and w denotes for the mass of the adsorbent (g).

The Langmuir isotherm can be represented by the following equation [LANGMUIR 1916]:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (2)$$

The linear form of the equation can be written as:

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

where: q_m denotes for the maximum adsorption capacity of the adsorbent to uptake adsorbate ($\text{mg}\cdot\text{g}^{-1}$), and K_L is the Langmuir constant ($\text{dm}^3\cdot\text{mg}^{-1}$).

The Freundlich isotherm can be represented by the following form [HERZOG 1909]:

$$q_e = K_F C_e^{1/n} \quad (4)$$

Which can be expressed in a linear form:

$$\log q_e = \frac{1}{n} \log C_e + \log K_F \quad (5)$$

where: q_e denotes for the equilibrium adsorption capacity of the adsorbent to uptake adsorbate (mg/g), C_e denotes for the equilibrium adsorbate concentration ($\text{mg}\cdot\text{dm}^{-3}$), and K_F and n are the Freundlich empirical parameters.

In this research work, a new trend of evaluation is being held to check the adsorption process when the amount of adsorbent is very low and its saturation is expected to occur. Thus, the two conventional isotherms will be checked to evaluate their relevance to the data.

ZEOLITE TUFF

The zeolite material used in this work is a natural Jordanian zeolite taken from Jebal Aritrain area which is located at North East Jordan and was first exploited in 1987. The Jordanian zeolite was entailed in many researches due to its unique characteristics [ABDLEHADI *et al.* 2001; AL-RASHDAN 1994; DWIRI 1987; IBRAHIM 1997; Jordan Cement Company 1985; MALABEH 1993].

The zeolite sample was ground and sifted; the remaining powder on the pan (size < 0.075 mm) was used in batch reactor experiment. In this experiment, the zeolite was prepared at the following doses: 2, 6, 10, 16, and 26 $\text{mg}\cdot\text{dm}^{-3}$.

X-ray diffraction analysis was conducted using powder X-ray diffractometer equipment at 40 kV and 20 mA. The zeolite sample is categorized as a Phillipsite rich tuff. It consisted of tetrahedral aluminosilicates bonded with replaceable alkaline sodium and potassium taking the structural form of $(\text{Na}_5\text{K}_6)(\text{Al}_{10}\text{Si}_{22}\text{O}_{64})\cdot 20\text{H}_2\text{O}$.

BET Specific surface area and pore volume were determined using a nitrogen sorption system Nova 2200e. True density was

measured by the Pentapyc 5200e. Cation-exchange capacity was determined using the Kjeldahl method, as described by KITSOPOULOS [1999]. In addition, the chemical composition of raw zeolite was obtained by X-ray fluorescence analysis. The physical and chemical properties of the zeolite material are summarized in Table 1.

Table 1. Physical and chemical properties of Jordanian zeolite tuff

Properties	Value
True density ($\text{g}\cdot\text{cm}^{-3}$)	2.68
Total pore volume ($\text{cm}^3\cdot\text{g}^{-1}$)	0.04
CEC ($\text{meq}\cdot\text{g}^{-1}$)	2.16
Specific surface area ($\text{m}^2\cdot\text{g}^{-1}$)	75
Oxides	
SiO ₂ (%)	42
Al ₂ O ₃ (%)	11.2
Fe ₂ O ₃ (%)	12.5
MgO (%)	9.4
CaO (%)	7.9
K ₂ O (%)	1.86
Na ₂ O (%)	1.54
TiO ₂ (%)	2.5

Explanations: CEC = cation-exchange capacity.
 Source: own elaboration.

Zeolite was immersed with (1 N) NaCl solution for 24 hours to replace all attached ions on it with (Na^+) ions. Zeolite was cleaned with distilled water (5 to 10) times, to remove all free (Cl^-) ions. Drops of (AgNO_3) were added to the zeolite soaked in distilled water to get rid of all free (Cl^-) as white precipitates.

NICKEL SOLUTION

Nickel stock solution was prepared using nickel sulphate salt (NiSO_4) having a molecular weight of ($154.76 \text{ g}\cdot\text{mol}^{-1}$) containing ($58.7 \text{ g}\cdot\text{mol}^{-1}$) of Ni (II). An amount of 0.5273 g of NiSO_4 salt was added to 1 dm^3 of distilled water to have a bulk solution of $200 \text{ mg}\cdot\text{dm}^{-3}$ of Ni concentration. The concentration of 200 ppm of Ni was then diluted with distilled water to obtain the required concentrations at the levels: 0.3, 0.4, 0.5, 0.7, 1, 2, 3, 4, and 5 ppm.

BATCH EXPERIMENTAL PROCEDURE

Batch reactors (500 cm^3 for each) were used for mixing specific doses of zeolite with different concentrations of nickel. By adding zeolite, the pH of the solution will rise up due to the release of alkaline metal ions from zeolite texture. Hence, the NiSO_4 salt was chosen to dampen the pH rise.

The pH was initially set to 4.5 and reached 5.2 at equilibrium showing maximum adsorption capacity. These information are compatible with researches performed on Ni removal by Jordanian zeolite [AL-ANBER *et al.* 2008; AL DWAIRI *et al.* 2012; ALI *et al.* 1997; ALLAWZI *et al.* 2010; BAKER *et al.* 2009].

For the batch adsorption processes, the zeolite was prepared with different low doses: 2, 6, 10, 16, and 26 $\text{mg}\cdot\text{dm}^{-3}$. Each zeolite concentration was tested with different initial nickel concentrations: 0.3, 0.4, 0.5, 0.7, 1, 2, 3, 4, and 5 ppm.

The samples were stirred continuously at 180 RPM for 24 hours at 20°C. After the stirring was complete, samples were allowed to clarify. Then the samples were filtrated using Whatman filter paper and kept cooled in a refrigerator. The nickel final concentration was finally measured using atomic absorption spectrometer (AAS).

RESULTS AND DISCUSSION

BATCH RESULTS

In this study, the binding of Ni onto zeolite is based on the cation exchange process between the Ni and the Na and K in the zeolite texture.

The pH of the solution is of a great importance for the partitioning during the treatment process. The ions of Ni start to precipitate in the form of hydroxides at pH around 6.5. However, low pH levels are not favoured for zeolite adsorption because this would upset the chemical structure of zeolite and thus reduce the adsorption capability. The pH was initially set to 4.5. By the addition of zeolite, the pH of the solution was raised due to the dissolution of alkali Na and K in the zeolite texture, and subsequently the pH reached 5.2 at equilibrium during stirring time. The final nickel constant concentrations of the samples in batch reactor at equilibrium are shown in Table 2.

Since the zeolite concentration is low, its adsorption capability will decrease after certain increase of initial nickel concentration as it will be approaching the saturation level. The adsorption of nickel onto zeolite increases primarily as the initial nickel concentration increases. However, the adsorbed nickel increases to a certain point and then tends to decrease by further increase of initial nickel concentration (Fig. 1). The behaviour of nickel removal by zeolite represented in Figure 1 shows that the percent of nickel removal reaches the maximum value and then tends to decrease for all zeolite concentrations. The optimal nickel removal reaches 65% when the initial nickel concentration is 1 ppm and the zeolite dose is 26 $\text{mg}\cdot\text{dm}^{-3}$. The point at which the maximum removal attained is given here a major concern, and is allocated as a peak point similar to those breakthrough points evolved with the time.

BEHAVIOUR OF NICKEL (NI) ACCORDING TO ADSORPTION ISOTHERMS ONTO LOW ZEOLITE DOSAGE

Primary evaluations of Ni adsorption for the whole experimental data presented in Table 2 have shown low relevance to Langmuir and Freundlich isotherms as that can be noticed by the values of the coefficient of determination for each zeolite concentration at varying initial Ni from 0.3 to 5.0 ppm (Tab. 3).

The two isotherms are different in concept in terms of homogeneous or heterogeneous surface, mono- or multi-layer adsorption, and finite or infinite saturation level. Consequently, the case in this study is to investigate the behaviour of the adsorption below and above the allocated peak point of nickel removal. In this insight, it is logical that the amount of adsorbed nickel and

Table 2. Equilibrium nickel concentrations at different zeolite doses and different initial Ni concentrations

Initial nickel concentration (ppm)	Equilibrium nickel concentration (ppm) ¹⁾ at zeolite dose				
	2 mg·dm ⁻³	6 mg·dm ⁻³	10 mg·dm ⁻³	16 mg·dm ⁻³	26 mg·dm ⁻³
0.3	0.26	0.23	0.19	0.17	0.16
0.4	0.27	0.24	0.21	0.19	0.19
0.5	0.25	0.23	0.22	0.21	0.21
0.7	0.32	0.30	0.28	0.27	0.26
1.0	0.43	0.40	0.38	0.37	0.35
2.0	1.01	0.97	0.94	0.84	0.75
3.0	1.75	1.73	1.68	1.43	1.21
4.0	2.53	2.50	2.44	2.26	2.05
5.0	3.40	3.38	3.30	3.27	3.11

¹⁾ The values are average values.

Source: own study.

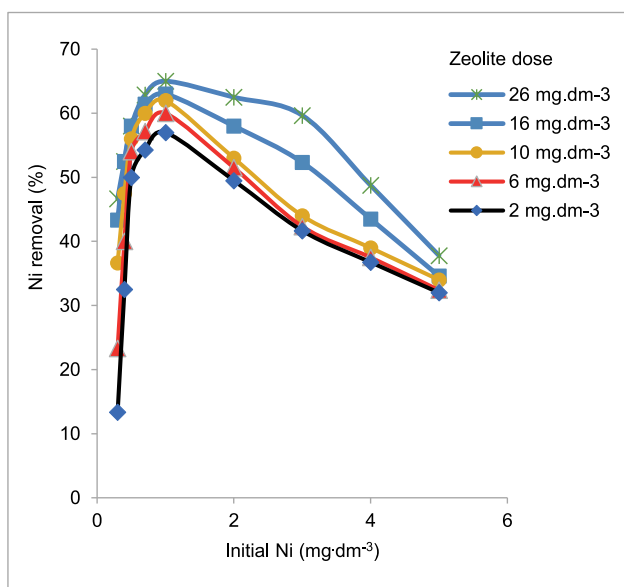


Fig. 1. Percent of nickel (Ni) removal with different initial Ni concentration and different zeolite doses; source: own study

adsorption energy are exponentially decreased upon the completion of adsorption process [ZELDOWITSCH 1934]. Different than Langmuir isotherm, one of the major disadvantages of the Freundlich isotherm is that it does not predict the adsorption maximum limit [SPARKS 2003]. Accordingly, the data was divided into two ranges depending on the theories of each isotherm and depending on the relevance of Ni adsorption data to each isotherm (Tab. 4, 5). The first range is assigned to Langmuir isotherm where the initial nickel concentrations are above 1 ppm. The other range is assigned to Freundlich isotherm where the initial nickel concentrations are below 1 ppm (Fig. 2).

The first range shows high relevance of data to Langmuir isotherm as that can be observed from the Figures 3. The highest R^2 of 0.9969 is associated with zeolite dosage at 10 ppm (Fig. 3c). The Langmuir equation permits the estimation of adsorption maximum limit. However, non-fitting results have been observed with the Langmuir equation at low adsorbate concentrations. The presence of many groups of adsorption sites with different affinities for adsorbate may be suggested to explain the observed behaviour

Table 3. Behaviour of Ni adsorption according to Langmuir-Freundlich isotherms for all data where the initial concentration is in the range of 0.3 to 5.0 ppm

Isotherm	Coefficient of determination (R^2) at zeolite dose				
	2 mg·dm ⁻³	6 mg·dm ⁻³	10 mg·dm ⁻³	16 mg·dm ⁻³	26 mg·dm ⁻³
Langmuir	0.03	0.02	0.39	0.59	0.56
Freundlich	0.54	0.59	0.68	0.67	0.67

Source: own study.

Table 4. Behaviour of Ni adsorption according to Langmuir-Freundlich isotherms for the data where the initial Ni concentration ≤ 1 ppm

Isotherm	Coefficient of determination (R^2) at zeolite dose				
	2 mg·dm ⁻³	6 mg·dm ⁻³	10 mg·dm ⁻³	16 mg·dm ⁻³	26 mg·dm ⁻³
Langmuir	bad negative fitting slope				
Freundlich	0.44	0.60	0.88	0.94	0.98

Source: own study.

Table 5. Behaviour of Ni adsorption according to Langmuir and Freundlich isotherms for the data where the initial Ni concentration ≥ 1 ppm

Isotherm	Coefficient of determination (R^2) at zeolite dose				
	2 mg·dm ⁻³	6 mg·dm ⁻³	10 mg·dm ⁻³	16 mg·dm ⁻³	26 mg·dm ⁻³
Langmuir	0.97	0.97	0.99	0.95	0.97
Freundlich	0.36	0.33	0.35	0.21	0.19

Source: own study.

[HOLFORD *et al.* 1974; SYERS *et al.* 1973]. Therefore, Langmuir interprets very well the data in the upper first range (Fig. 3), while it does not so in the lower second range. However, if there are different types of active sites, micromeritics analysis and BET studies are strongly recommend for future studies.

The capacity (q_m) of zeolite at the best fit is estimated to be $222.2 \text{ mg}\cdot\text{g}^{-1}$ with Langmuir constant K_L of $0.98 \text{ dm}^3\cdot\text{mg}^{-1}$. The K_L plays a role in Langmuir characterization by a dimensionless constant defined as a separation constant, R_L that can be identified in the following equation [WEBBER 1974]:

$$R_L = \frac{1}{1 + K_L C_o} \quad (7)$$

where: K_L denotes for the Langmuir constant, and C_o denotes for the initial adsorbate concentration ($\text{mg}\cdot\text{dm}^{-3}$). In this perspective, the adsorption is considered unfavourable if the value of R_L is greater than 1, linear if the R_L equals 1, favourable if the R_L is between 0 and 1, and irreversible if the R_L equals 0.

As per the results obtained in this work, the separation constant (R_L) is in the range from 0.17 to 0.51 for the of initial Ni concentrations range, which shows favourable adsorption process.

The second range shows less relevance of data to Freundlich isotherm at zeolite doses below $10 \text{ mg}\cdot\text{dm}^{-3}$ as shown in the Figures 4a and 4b. This can be explained as that the experiments produced

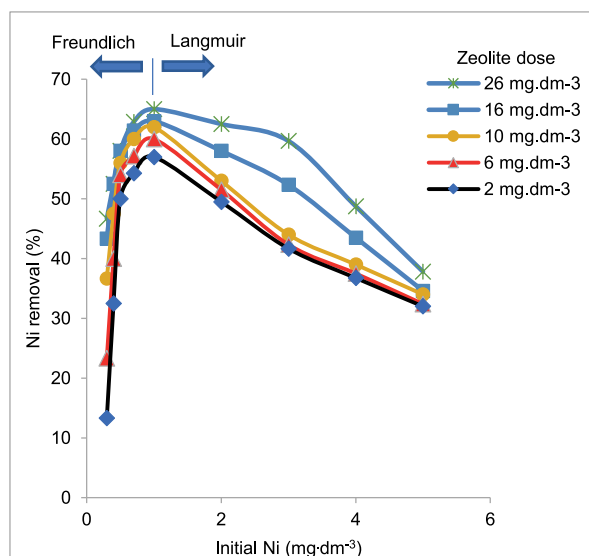


Fig. 2. Domains where Langmuir and Freundlich isotherms are allocated; source: own study

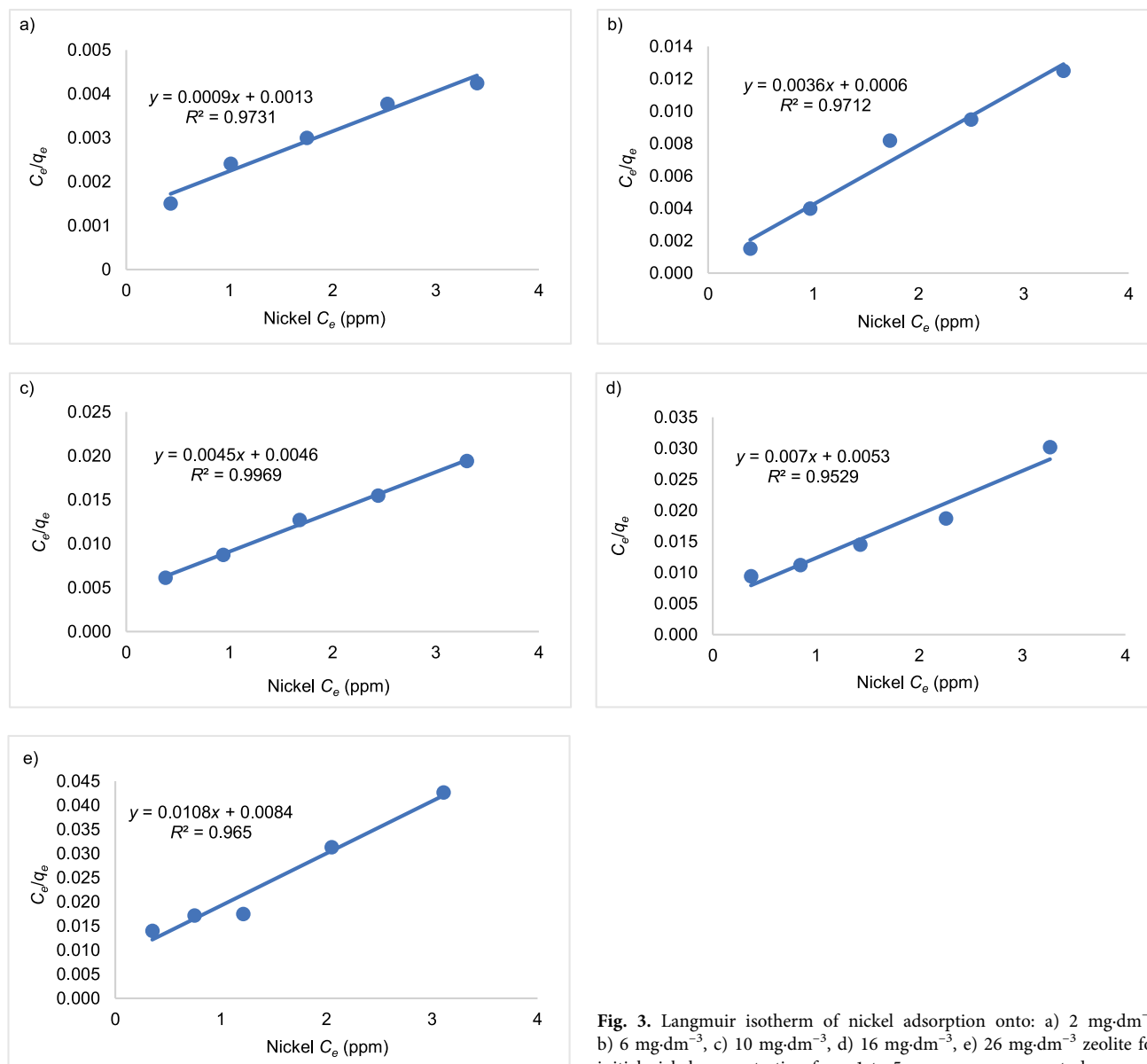


Fig. 3. Langmuir isotherm of nickel adsorption onto: a) $2 \text{ mg}\cdot\text{dm}^{-3}$, b) $6 \text{ mg}\cdot\text{dm}^{-3}$, c) $10 \text{ mg}\cdot\text{dm}^{-3}$, d) $16 \text{ mg}\cdot\text{dm}^{-3}$, e) $26 \text{ mg}\cdot\text{dm}^{-3}$ zeolite for initial nickel concentration from 1 to 5 ppm; source: own study

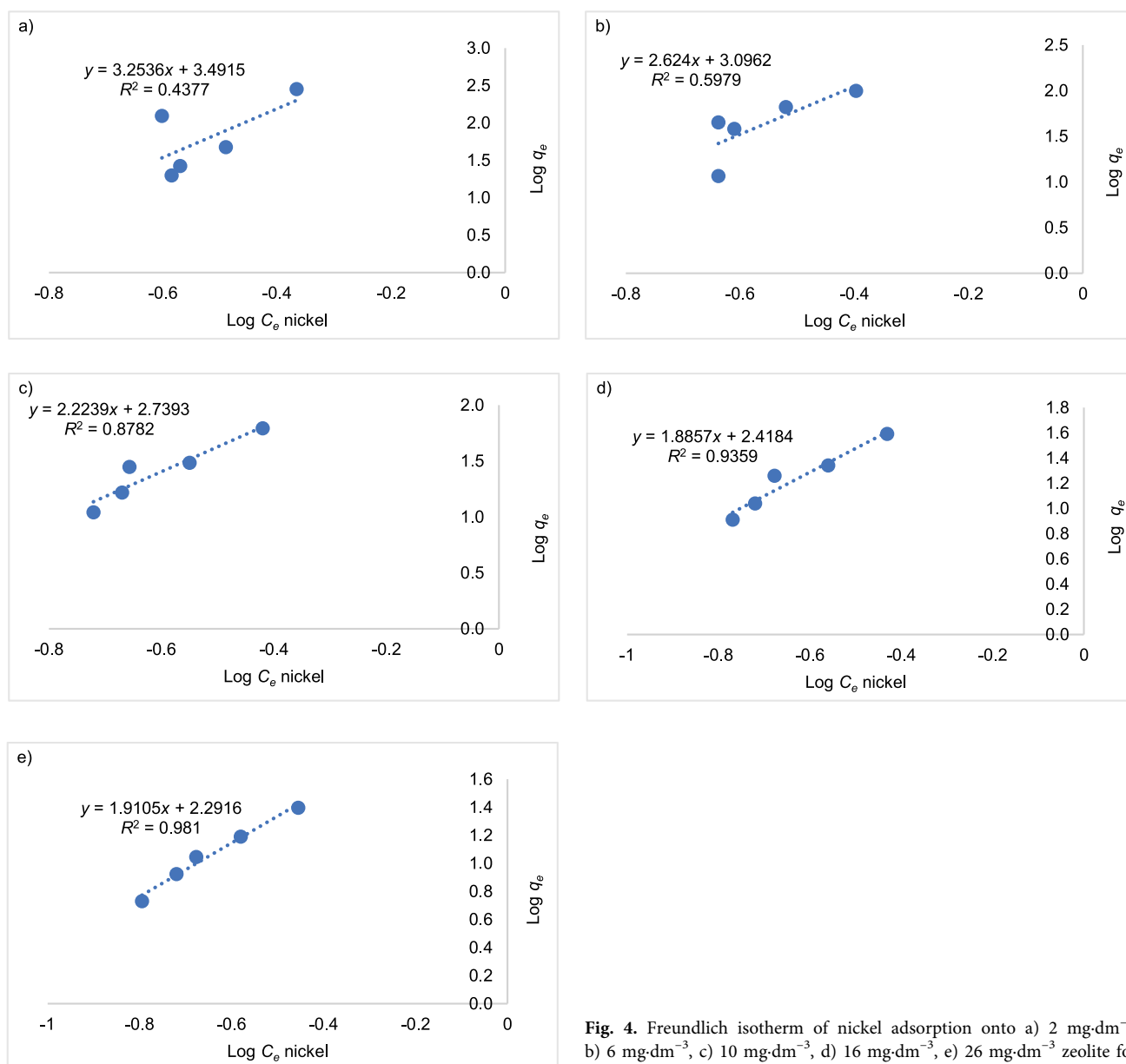


Fig. 4. Freundlich isotherm of nickel adsorption onto a) $2 \text{ mg}\cdot\text{dm}^{-3}$, b) $6 \text{ mg}\cdot\text{dm}^{-3}$, c) $10 \text{ mg}\cdot\text{dm}^{-3}$, d) $16 \text{ mg}\cdot\text{dm}^{-3}$, e) $26 \text{ mg}\cdot\text{dm}^{-3}$ zeolite for initial nickel concentration from 0.3 to 1 ppm; source: own study

imprecise isotherm interpretation at which a saturation behaviour is approached and thus it is recommended to apply Freundlich isotherm to a lower adsorbate concentration [RUSHTON *et al.* 2005], or higher adsorbent dose since this implies the same logic when the adsorbent dose is very low and the saturation behaviour is getting approached. Hence, a high relevance of data to Freundlich isotherm is observed while the adsorbent dose exceeds $10 \text{ mg}\cdot\text{dm}^{-3}$ (Fig. 4). The highest R^2 of 0.98 is associated with zeolite dosage at $26 \text{ mg}\cdot\text{dm}^{-3}$ (Fig. 4e). These results show a limitation to the Freundlich isotherm as it does not describe a capacity bound in the adsorption process [SUZUKI 1990].

The Freundlich empirical constant, K_F represents the adsorbent capacity, while n constant denotes for adsorption intensity. The $1/n$ value is located in the range from 0 to 1, where it will be more heterogeneous as its value gets closer to zero.

A cooperative adsorption is expected to occur when the value of $1/n$ is greater than 1 [FYTIANOS *et al.* 2000]. K_F and n , are estimated to be 195.7 and 0.52 respectively, and the $1/n$ value equals 1.91 for the best fit when zeolite dose is $26 \text{ mg}\cdot\text{dm}^{-3}$.

The presence of many groups of adsorption sites with different affinities for adsorbate may be suggested to explain the adsorption behaviour. However, if there are different types of active sites, micromeritics analysis and BET studies are strongly recommended for future studies. In addition, a study of hydration may be carried out to support adsorbent cation exchange capacity and selectivity.

Supplementary information is needed to explore reversibility or irreversibility of sorbed metals on the zeolite and also additional studies are needed to know the causes of the hysteresis in the sorption-desorption of metals on the zeolite.

CONCLUSIONS

Experimental work has been conducted to explore the behaviour of nickel adsorption from waters onto very low dose of natural Jordanian zeolite according to Langmuir and Freundlich isotherms. When the zeolite concentration is very low in the batch reactor, it will tend to be saturated with the adsorbate Ni, so the removal efficiency of zeolite reaches peak point and then goes down by increasing Ni concentration. At this level of low zeolite dose, the adsorption follows neither Freundlich nor Langmuir isotherms; it rather follows the Freundlich for the data plot just below the peak point, whereas it follows Langmuir for the plot just above that point. Consequently, the findings here about the adsorption behaviour of nickel at low zeolite concentrations provide new information to the scientific knowledge and help tuning water treatment techniques.

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