JOURNAL OF WATER AND LAND DEVELOPMENT

e-ISSN 2083-4535

Polish Academy of Sciences (PAN) Institute of Technology and Life Sciences – National Research Institute (ITP – PIB)

JOURNAL OF WATER AND LAND DEVELOPMENT
DOI: 10.24425/jwld.2021.138170
2021, No. 50 (VI–IX): 150–157

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

Ziad Al-Ghazawi[1)], Ahmad Qasaimeh[1)] ✉, Bilal Al-Bataina[2)]

[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].

© 2021. The Authors. Published by Polish Academy of Sciences (PAN) and Institute of Technology and Life Sciences – National Research Institute (ITP – PIB).
This is an open access article under the CC BY-NC-ND license (https://creativecommons.org/licenses/by-nc-nd/3.0/)

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 multilayer 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:

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

where: q_e denotes for the equilibrium adsorption capacity of the adsorbent to uptake adsorbate (mg·g^{-1}); C_o denotes for the initial adsorbate concentration (mg·dm^{-3}), C_e denotes for the equilibrium adsorbate concentration (mg·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]:

$$q_e = \frac{q_m K_{\mathrm{L}} C_e}{1 + K_{\mathrm{L}} C_e} \tag{2}$$

The linear form of the equation can be written as:

$$\frac{C_e}{q_e} = \frac{1}{K_{\mathrm{L}} q_m} + \frac{C_e}{q_m} \tag{3}$$

where: q_m denotes for the maximum adsorption capacity of the adsorbent to uptake adsorbate (mg·g^{-1}), and K_{L} is the Langmuir constant (dm^3·mg^{-1}).

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

$$q_e = K_{\mathrm{F}} C_e^{1/n} \tag{4}$$

Which can be expressed in a linear form:

$$\log q_e = \frac{1}{n} \log C_e + \log K_{\mathrm{F}} \tag{5}$$

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 (mg·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 mg·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 $(Na_5K_6)(Al_{10}Si_{22}O_{64})\cdot 20H_2O$.

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

© 2021. The Authors. Published by Polish Academy of Sciences (PAN) and Institute of Technology and Life Sciences – National Research Institute (ITP – PIB).
This is an open access article under the CC BY-NC-ND license (https://creativecommons.org/licenses/by-nc-nd/3.0/)

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 ($g \cdot cm^{-3}$)	2.68
Total pore volume ($cm^3 \cdot g^{-1}$)	0.04
CEC ($meq \cdot g^{-1}$)	2.16
Specific surface area ($m^2 \cdot g^{-1}$)	75
Oxides	
SiO_2 (%)	42
Al_2O_3 (%)	11.2
Fe_2O_3 (%)	12.5
MgO (%)	9.4
CaO (%)	7.9
K_2O (%)	1.86
Na_2O (%)	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 $g \cdot mol^{-1}$) containing (58.7 $g \cdot mol^{-1}$) 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 $mg \cdot dm^{-3}$ 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 $mg \cdot dm^{-3}$. 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 $mg \cdot dm^{-3}$. 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

© 2021. The Authors. Published by Polish Academy of Sciences (PAN) and Institute of Technology and Life Sciences – National Research Institute (ITP – PIB).
This is an open access article under the CC BY-NC-ND license (https://creativecommons.org/licenses/by-nc-nd/3.0/)

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.

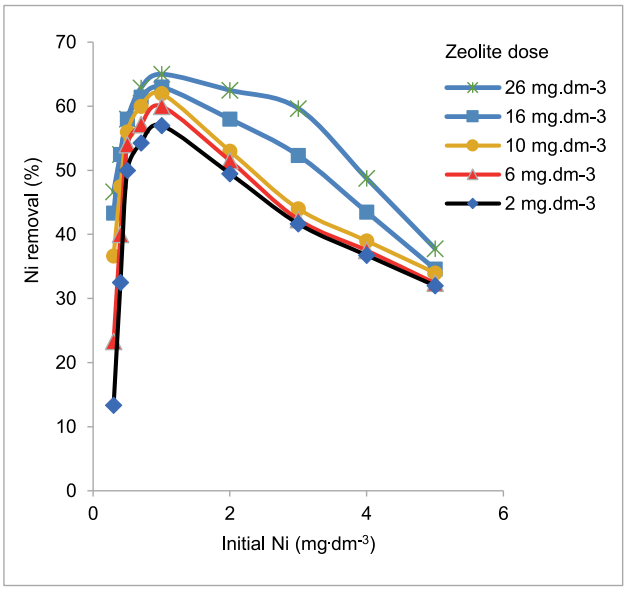

Fig. 1. Percent of nickel (Ni) removal with different initial Ni concentration and different zeolite doses; source: own study

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 [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.

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 ≥1ppm

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.

© 2021. The Authors. Published by Polish Academy of Sciences (PAN) and Institute of Technology and Life Sciences – National Research Institute (ITP – PIB).
This is an open access article under the CC BY-NC-ND license (https://creativecommons.org/licenses/by-nc-nd/3.0/)

The capacity (q_m) of zeolite at the best fit is estimated to be 222.2 mg·g^{-1} with Langmuir constant K_L of 0.98 dm^3·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]:

$$R_L = \frac{1}{1 + K_L C_o} \tag{7}$$

where: K_L denotes for the Langmuir constant, and C_o denotes for the initial adsorbate concentration (mg·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 mg·dm^{-3} as shown in the Figures 4a and 4b. This can be explained as that the experiments produced

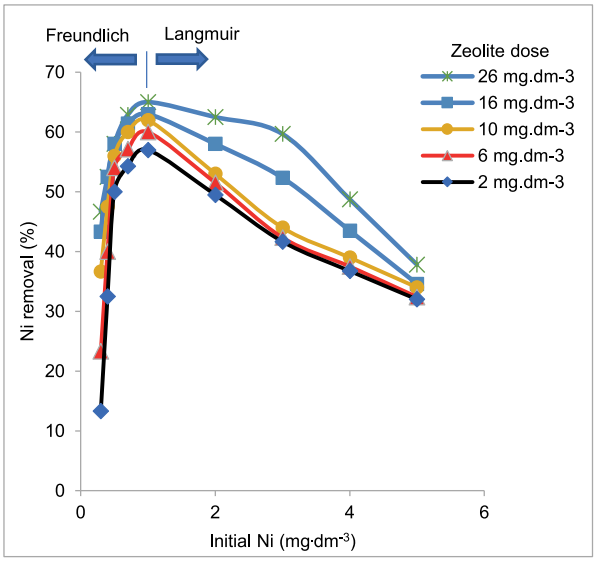

Fig. 2. Domains where Langmuir and Freundlich isotherms are allocated; source: own study

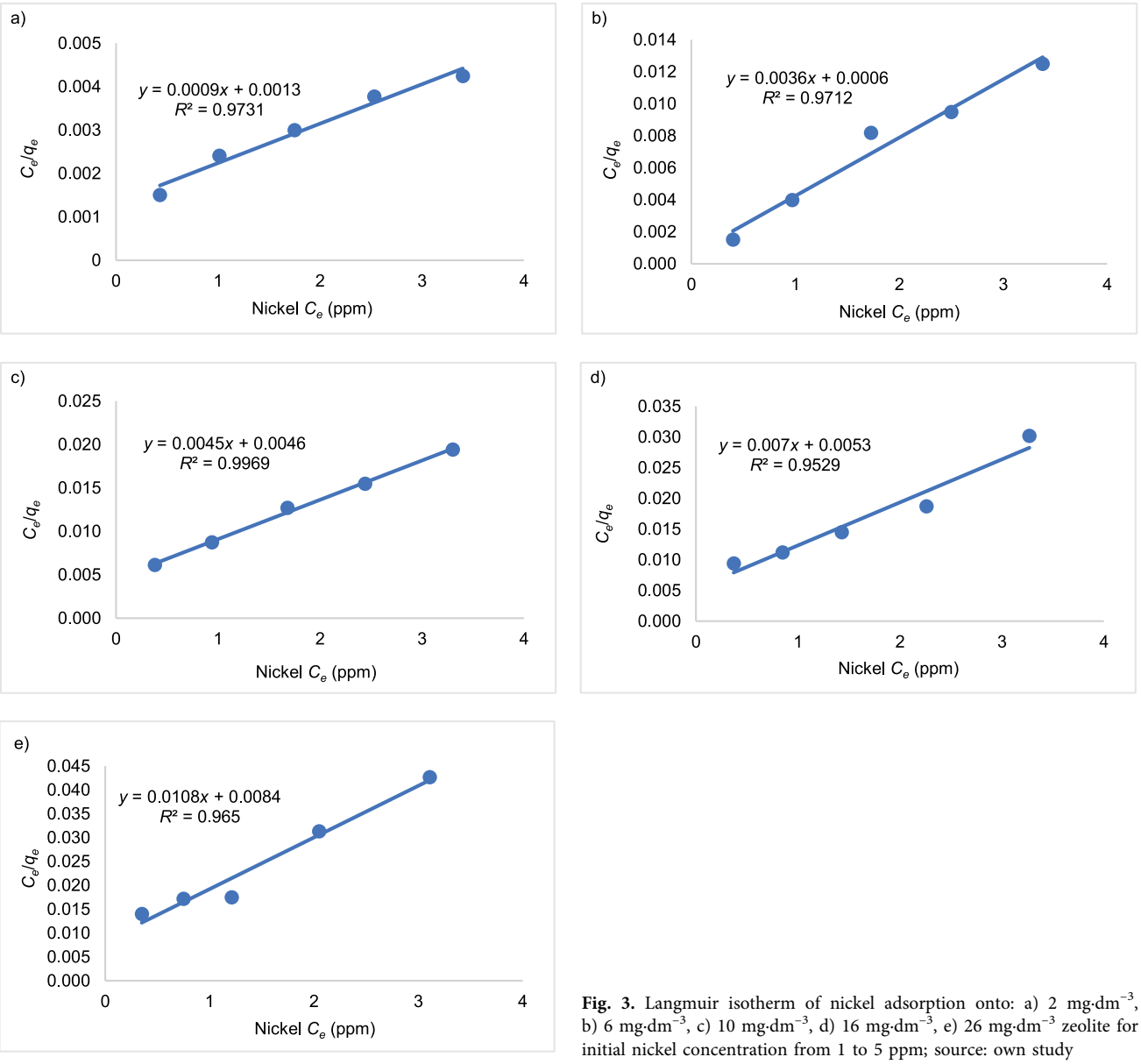

Fig. 3. Langmuir isotherm of nickel adsorption onto: a) 2 mg·dm^{-3}, b) 6 mg·dm^{-3}, c) 10 mg·dm^{-3}, d) 16 mg·dm^{-3}, e) 26 mg·dm^{-3} zeolite for initial nickel concentration from 1 to 5 ppm; source: own study

© 2021. The Authors. Published by Polish Academy of Sciences (PAN) and Institute of Technology and Life Sciences – National Research Institute (ITP – PIB).
This is an open access article under the CC BY-NC-ND license (https://creativecommons.org/licenses/by-nc-nd/3.0/)

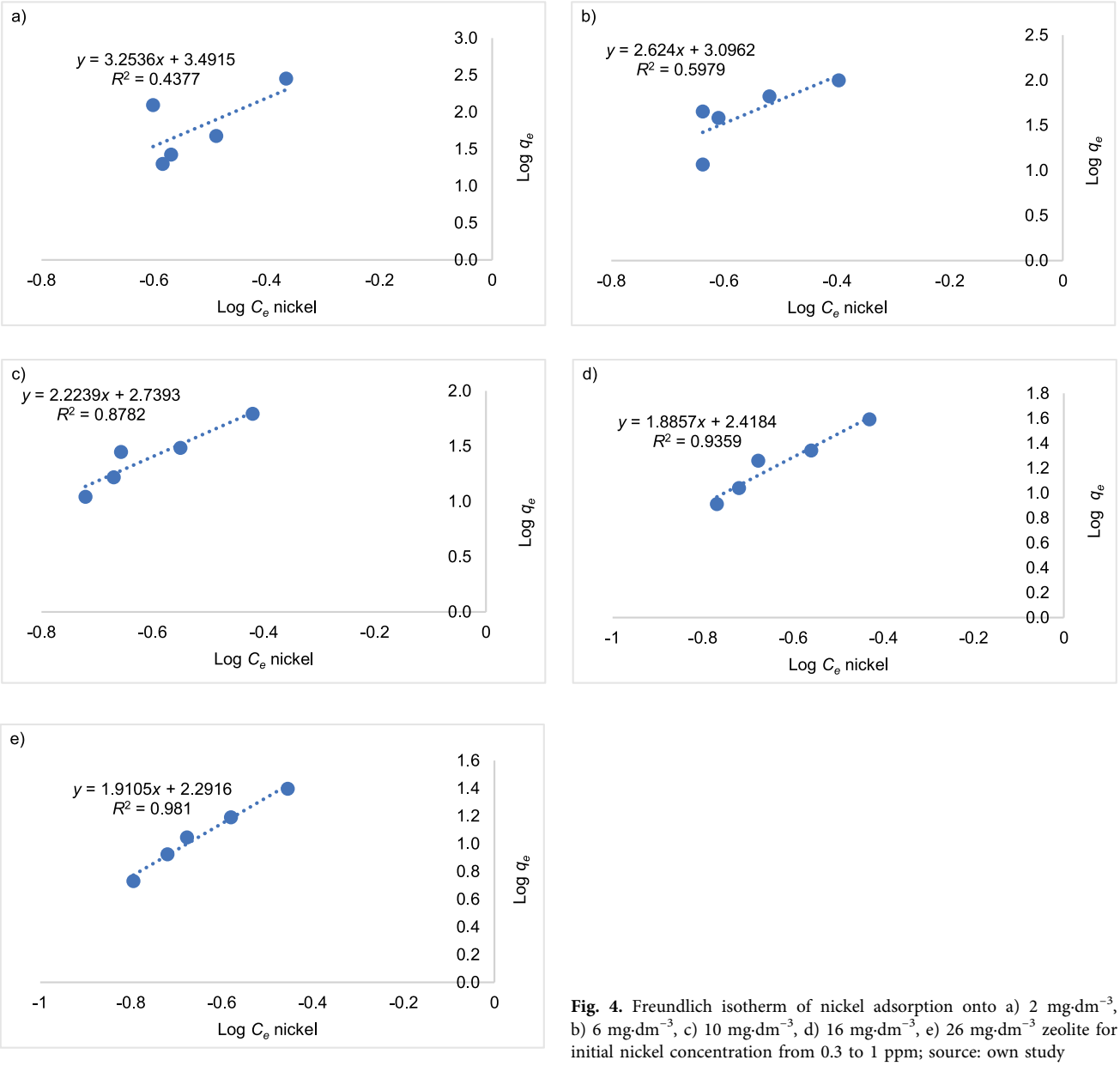

Fig. 4. Freundlich isotherm of nickel adsorption onto a) 2 mg·dm^{-3}, b) 6 mg·dm^{-3}, c) 10 mg·dm^{-3}, d) 16 mg·dm^{-3}, e) 26 mg·dm^{-3} zeolite for initial nickel concentration from 0.3 to 1 ppm; source: own study

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 mg·dm^{-3} (Fig. 4). The highest R^2 of 0.98 is associated with zeolite dosage at 26 mg·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 mg·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.

© 2021. The Authors. Published by Polish Academy of Sciences (PAN) and Institute of Technology and Life Sciences – National Research Institute (ITP – PIB).
This is an open access article under the CC BY-NC-ND license (https://creativecommons.org/licenses/by-nc-nd/3.0/)

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.

REFERENCES

Adamson A.W., Gast A.P. 1967. Physical chemistry of surfaces. Vol. 150 pp. 180. New York. Interscience publishers.

Al Dwairi R., Al-Rawajfeh A. 2012. Removal of cobalt and nickel from wastewater by using Jordan low-cost zeolite and bentonite. Journal of the University of Chemical Technology and Metallurgy. Vol. 47(1) p. 69–76.

Al-Anber M., Al-Anber Z.A. 2008. Utilization of natural zeolite as ion-exchange and sorbent material in the removal of iron. Desalination. Vol. 225(1–3) p. 70–81. DOI 10.1016/j.desal.2007.07.006.

Al-Jabari M., Abualfailat M., Shaheen S. 2012. Treating leather tanning wastewater with stone cutting solid waste. Clean Soil Air Water. Vol. 40(2) p. 206–210. DOI 10.1002/CLEN.201000431.

Al-Jabari M., Zahdeh N., Iqefan N., Dweik H. 2015. Technical feasibility of treating dairy wastewater with natural low cost adsorbents. International Journal of Environment and Water. Vol. 4(4) p. 31–39.

Al-Jabari M. 2016. Kinetic models for adsorption on mineral particles comparison between Langmuir kinetics and mass transfer. Environmental Technology & Innovation. Vol. 6 p. 27–37. DOI 10.1016/j.eti.2016.04.005.

Al-Jabari M. 2017. Kinetic mass transfer adsorption model for treating dairy wastewater with stone cutting solid waste. Environmental Technology & Innovation. Vol. 7 p. 21–29. DOI 10.1016/j.eti.2016.11.004.

Al-Rashdan Z.A.F. 1994. Treatment of domestic waste water effluent from stabilization ponds using Jordanian zeolitic tuffs. MSc Thesis. Yarmouk University, Jordan. pp. 218.

Ali A.A.H., El-Bishtawi R. 1997. Removal of lead and nickel ions using zeolite tuff. Journal of Chemical Technology & Biotechnology. Vol. 69(1) p. 27–34. DOI 10.1002/(SICI)1097-4660(199705)69:1<27::AID-JCTB682>3.0.CO;2-J.

Allawzi M., Al-Asheh S. 2010. Use of Jordanian natural zeolite as sorbent for removal of cadmium from aqueous solutions. Desalination and Water Treatment. Vol. 22(1–3) p. 349–354. DOI 10.5004/dwt.2010.1200.

Babel S., Kurniawan T.A. 2003. Low-cost adsorbents for heavy metals uptake from contaminated water: A review. Journal of Hazardous Materials. Vol. 97 p. 219–243. DOI 10.1016/S0304-3894(02)00263-7.

Baker H.M., Massadeh A.M., Younes H.A. 2009. Natural Jordanian zeolite: removal of heavy metal ions from water samples using column and batch methods. Environmental Monitoring and Assessment. Vol. 157(1–4) p. 319–330. DOI 10.1007/s10661-008-0537-6.

Crini G. 2005. Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. Progress in Polymer Science. Vol. 30 p. 38–70. DOI 10.1016/j.progpolymsci.2004.11.002.

Crini G. 2006. Non-conventional low-cost adsorbents for dye removal: A review. Bioresource Technology. Vol. 97 p. 1061–1085. DOI 10.1016/j.biortech.2005.05.001.

De Aguiar M.R.M.P., Novaes A.C., Guarino A.W.S. 2002. Removal of heavy metals from wastewaters by aluminosilicate. Quimica Nova. Vol. 25 p. 1145–1154.

Demirbas E., Kobya M., Konukman A.E.S. 2008. Error analysis of equilibrium studies for the almond shell activated carbon adsorption of Cr(VI) from aqueous solutions. Journal of Hazardous Materials. Vol. 154 p. 787–794. DOI 10.1016/j.jhazmat.2007.10.094.

Dwiri I. 1987. A chemical study of the Palagonitic Tuff of Artian area of Jordan with special references to nature, origin and industrial potential of associated zeolite deposits. PhD Thesis. Hull University, UK pp. 408.

El-Hamed S., Abdlehadi N. 2001. Engineering properties of basalt for constructions use. Natural Resources Authority (Internal Report) pp. 32.

Feng N., Guo X., Sha L. 2009. Adsorption study of copper (II) by chemically modified orange peel. Journal of Hazardous Materials. Vol. 164 p. 1286–1292. DOI 10.1016/j.jhazmat.2008.09.096.

Freundlich H.M.F. 1906. Over the adsorption in solution. The Journal of Physical Chemistry. Vol. 57 p. 385–471.

Fytianos K., Voudrias E., Kokkalis E. 2000. Sorption–desorption behavior of 2, 4-dichlorophenol by marine sediments. Chemosphere. Vol. 40 p. 3–6. DOI 10.1016/s0045-6535(99)00214-3.

Gonzalez S., Lopez-Roldan R., Cortina J.L. 2013. Presence of metals in drinking water distribution networks due to pipe material leaching: A review. Toxicological and Environmental Chemistry. Vol. 95(6) p. 870–889. DOI 10.1080/02772248.2013.840372.

Güzel F., Sayğilib H., Sayğilia G.A., Koyuncua F. 2015. New low-cost nanoporous carbonaceous adsorbent developed from carob (*Ceratonia siliqua*) processing industry waste for the adsorption of anionic textile dye: Characterization, equilibrium and kinetic modeling. Journal of Molecular Liquids. Vol. 206 p. 244–255. DOI 10.1016/j.molliq.2015.02.037.

Hedstrom A. 2001. Ion exchange of ammonium in zeolites: A literature review. Journal of Environmental Engineering. Vol. 127 p. 673–681. DOI 10.1061/(ASCE)0733-9372(2001)127:8(673).

Heikkinen P., Korkka-Niemi K., Lahti M., Salonen V.P. 2002. Groundwater and surface water contamination in the area of the Hitura nickel mine, Western Finland. Environmental Geology. Vol. 42(4) p. 313–329. DOI 10.1007/s00254-002-0525-z.

Herzog R.O. 1909. Kapillarchemie, eine Darstellung der Chemie der Kolloide und verwandter Gebiete. Von Dr. Herbert Freundlich. [Capillary and colloid chemistry]. Leipzig. Verlag der Akademischen Verlagsgesellschaft pp. 591.

Holford I.C.R., Wedderburn R.W.M., Mattingly G.E.G. 1974. A Langmuir two-surface equation as a model for phosphate adsorption by soils. Journal of Soil Science. Vol. 25 p. 242–255. DOI 10.1111/j.1365-2389.1974.tb01121.x.

Ibrahim K. 1997. Geology of Al-Bashiryeh (Aritayn), map no. II-3354. Natural Resources Authority. Geology of Al-Azraq, map no. I-3553. Natural Resources Authority. Bulletin no. 36.

Imaga C., Abia A. 2015. Adsorption kinetics and mechanisms of Ni2+ sorption using carbonized and modified sorghum (*Sorghum*

© 2021. The Authors. Published by Polish Academy of Sciences (PAN) and Institute of Technology and Life Sciences – National Research Institute (ITP – PIB).
This is an open access article under the CC BY-NC-ND license (https://creativecommons.org/licenses/by-nc-nd/3.0/)

bicolor) hull of two pore sizes (150 μm and 250 μm): A comparative study. International Journal of Chemical Studies. Vol. 2 (5) p. 59–68.

Jordan Cement Company 1985. Cement industry and raw materials used. Seminar on Mining Industries. Arab Engineers Union and Jordan Engineers Association. Amman, Jordan 23–25.09.1985 pp. 42.

Kitsopoulos K.P. 1999. Cation-exchange capacity (CEC) of zeolitic volcaniclastic materials: Applicability of the ammonium acetate saturation (AMAS) method. Clays and Clay Minerals. Vol. 47 p. 688–696. DOI 10.1346/CCMN.1999.0470602.

Korkuna O., Leboda R., Skubiszewska-Zięba J., Vrublevs'ka T., Gun'ko V.M., Ryczkowski J. 2006. Structural and physicochemical properties of natural zeolites: clinoptilolite and mordenite. Microporous and Mesoporous Materials. Vol. 87 p. 243–254. DOI 10.1016/j.micromeso.2005.08.002.

Kundu S., Gupta A.K. 2006. Arsenic adsorption onto iron oxide-coated cement (IOCC): regression analysis of equilibrium data with several isotherm models and their optimization. Chemical Engineering Journal. Vol. 122 p. 93–106. DOI 10.1016/j.cej.2006.06.002.

Langmuir I. 1916. The constitution and fundamental properties of solids and liquids. Journal of the American Chemical Society. Vol. 38(11) p. 2221–2295. DOI 10.1021/ja02268a002.

Malabeh A. 1993. The volcanology, mineralogy and geochemistry of selected pyroclastic cones from NE Jordan and their evaluation for possible industrial applications. PhD Thesis. Universitat Erlangen. Germany.

Mercer B.W., Ames L.L. 1978. Zeolite ion exchange in radioactive and municipal wastewater treatment. In: Natural zeolites: occurrence, properties, use. Eds. L.B. Sand, F.A. Mumpton. Elmsford, New York, Oxford. Pergamon Press. p. 451–462.

Mittal H., Maity A., Sinha Ray S. 2015. The adsorption of Pb^{2+} and Cu^{2+} onto gum ghatti-grafted poly(acrylamide-co-acrylonitrile) biodegradable hydrogel: Isotherms and kinetic models. The Journal of Physical Chemistry. B. Vol. 119(5) p. 2026–2039. DOI 10.1021/jp5090857.

Mumpton F. 1978. Natural zeolites. A new industrial mineral commodity. In: Natural zeolites: occurrence, properties, use. Eds. L.B. Sand, F.A. Mumpton. Elmsford, New York, Oxford. Pergamon Press p. 3–30.

Pollard S.J.T., Fowler G.D., Sollars C.J., Perry R. 1992. Low-cost adsorbents for waste and waste-water treatment: a review. Science of the Total Environment. Vol. 116 p. 31–52. DOI 10.1016/0048-9697(92)90363-W.

Rushton G.T., Karns C.L., Shimizu K.D. 2005. A critical examination of the use of the Freundlich isotherm in characterizing molecularly imprinted polymers (MIPs). Analytica Chimica Acta. Vol. 528 (1) p. 107–113. DOI 10.1016/j.aca.2004.07.048.

Shafeeyan M.S., Wan Daud W.M.A., Shamiri A. 2014. A review of mathematical modeling of fixed-bed columns for carbon dioxide adsorption. Chemical Engineering Research and Design. Vol. 92 (5) p. 961–988. DOI 10.1016/j.cherd.2013.08.018.

Sparks D.L. 2003. Environmental soil chemistry. Elsevier. ISBN 978-0-12-656446-4 pp. 151.

Suzuki M. 1990. Adsorption engineering. Tokyo. Elsevier Science. ISBN 978-0-44-498802-7 pp. 306.

Syers J.K., Browman M.G., Smillie G.W., Corey R.B. 1973. Phosphate sorption by soils evaluated by the Langmuir adsorption equation. Soil Science Society of America Journal. Vol. 37 p. 358–363. DOI 10.2136/sssaj1973.03615995003700030015x.

Tóth G., Hermann T., Da Silva M.R., Montanarella L. 2016. Heavy metals in agricultural soils of the European Union with implications for food safety. Environment International. Vol. 88 p. 299–309. DOI 10.1016/j.envint.2015.12.017.

Vareda P., Valente A.J.M., Durães L. 2019. Assessment of heavy metal pollution from anthropogenic activities and remediation strategies: A review. Journal of Environmental Management. Vol. 246 p. 101–118. DOI 10.1016/j.jenvman.2019.05.126.

Vhahangwele M., Khathutshelo L.M. 2018. Environmental contamination by heavy metals. In: Heavy metals. Eds. H. Saleh, R. Aglan. Vol. 10 p. 115–132. DOI 10.5772/intechopen.76082.

Vijayaraghavan K., Padmesh T.V.N., Palanivelu K., Velan M. 2016. Biosorption of nickel (II) ions onto Sargassum wightii: application of two-parameter and three parameter isotherm models. Journal of Hazardous Materials. Vol. B133 p. 304–308. DOI 10.1016/j.jhazmat.2005.10.016.

Wang S., Ang H.M., Tadé M.O. 2008. Novel applications of red mud as coagulant, adsorbent and catalyst for environmentally benign processes. Chemosphere. Vol. 72 p. 1621–1635. DOI 10.1016/j.chemosphere.2008.05.013.

Wang S.B., Wu H.W. 2006. Environmental-benign utilisation of fly ash as low-cost adsorbents. Journal of Hazardous Materials. Vol. 136 p. 482–501. DOI 10.1016/j.jhazmat.2006.01.067.

Webber T.W., Chakkravorti R.K. 1974. Pore and solid diffusion models for fixed-bed adsorbers, AlChE Journal. Vol. 20 p. 228–238. DOI 10.1002/aic.690200204.

Wyciszkiewicz M., Saeid A., Malinowski P., Chojnacka K. 2017. Valorization of phosphorus secondary raw materials by acidithiobacillus ferrooxidans. Molecules. Vol. 22 pp. 473. DOI 10.3390/molecules22030473.

Xia L.X., Shen Z., Vargas T., Sun W.J., Ruan R.M., Xie Z.D., Qiu G.Z. 2013. Attachment of acidithiobacillus ferrooxidans onto different solid substrates and fitting through Langmuir and Freundlich equations. Biotechnology Letters. Vol. 35 p. 2129–2136. DOI 10.1007/s10529-013-1316-1.

Xu Z., Cai J.-G., Pan B.C. 2013. Mathematically modeling fixed-bed adsorption in aqueous systems. Journal of Zhejiang University SCIENCE A. Vol. 14 p. 155–176. DOI 10.1631/jzus.A1300029.

Zeldowitsch J. 1934. Adsorption site energy distribution. Acta Physicochimica URSS. Vol. 1 p. 961–973

Zhang W., Li Q., Cong J., Wei B., Wang S. 2018. Mechanism analysis of selective adsorption and specific recognition by molecularly imprinted polymers of Ginsenoside Re. Polymers. Vol. 10(2) pp. 216. DOI 10.3390/polym10020216.

© 2021. The Authors. Published by Polish Academy of Sciences (PAN) and Institute of Technology and Life Sciences – National Research Institute (ITP – PIB).
This is an open access article under the CC BY-NC-ND license (https://creativecommons.org/licenses/by-nc-nd/3.0/)