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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 (R²) 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 (R²) 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], and natural and artificial zeolites [BABEL et al. 2003; HEIDSTROM 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 [Guzel 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; Wyciszkiwicz 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. 2006]. 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].

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

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$$

(2)

The linear form of the equation can be written as:

$$\frac{C_e}{q_e} = \frac{1}{K_Lq_m} + \frac{C_e}{q_m}$$

(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]:

$$q_e = K_F C_e^{1/n}$$

(4)

Which can be expressed in a linear form:

$$\log q_e = \frac{1}{n} \log C_e + \log K_F$$

(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$^{-3}$), $K_F$ 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 Jebel Artrain 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$\alpha$K$\alpha$)($Al_{10}Si_{12}O_{30}$)-20H$\alpha$O.

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

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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

<table>
<thead>
<tr>
<th>Oxides</th>
<th>Value (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO2</td>
<td>42</td>
</tr>
<tr>
<td>Al2O3</td>
<td>11.2</td>
</tr>
<tr>
<td>Fe2O3</td>
<td>12.5</td>
</tr>
<tr>
<td>MgO</td>
<td>9.4</td>
</tr>
<tr>
<td>CaO</td>
<td>7.9</td>
</tr>
<tr>
<td>K2O</td>
<td>1.86</td>
</tr>
<tr>
<td>Na2O</td>
<td>1.54</td>
</tr>
<tr>
<td>TiO2</td>
<td>2.5</td>
</tr>
</tbody>
</table>

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 (AgNO3) were added to the zeolite soaked in distilled water (5 to 10) times, to remove all free alkaline metal ions from zeolite texture. Hence, the NiSO4 salt was chosen to dampen the pH rise. The pH was initially set to 4.5 and 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.

For the batch adsorption processes, the zeolite was prepared with different low doses: 2, 6, 10, 16, and 26 mg∙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∙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
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 2. Equilibrium nickel concentrations at different zeolite doses and different initial Ni concentrations

<table>
<thead>
<tr>
<th>Initial nickel concentration (ppm)</th>
<th>Equilibrium nickel concentration (ppm)(^1) at zeolite dose</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2 mg dm(^{-3})</td>
</tr>
<tr>
<td>0.3</td>
<td>0.26</td>
</tr>
<tr>
<td>0.4</td>
<td>0.27</td>
</tr>
<tr>
<td>0.5</td>
<td>0.25</td>
</tr>
<tr>
<td>0.7</td>
<td>0.32</td>
</tr>
<tr>
<td>1.0</td>
<td>0.43</td>
</tr>
<tr>
<td>2.0</td>
<td>1.01</td>
</tr>
<tr>
<td>3.0</td>
<td>1.75</td>
</tr>
<tr>
<td>4.0</td>
<td>2.53</td>
</tr>
<tr>
<td>5.0</td>
<td>3.40</td>
</tr>
</tbody>
</table>

\(^1\) The values are average values. Source: own study.

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

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Coefficient of determination ($R^2$) at zeolite dose</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2 mg dm(^{-3})</td>
</tr>
<tr>
<td>Langmuir</td>
<td>0.03</td>
</tr>
<tr>
<td>Freundlich</td>
<td>0.54</td>
</tr>
</tbody>
</table>

Source: own study.

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

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Coefficient of determination ($R^2$) at zeolite dose</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2 mg dm(^{-3})</td>
</tr>
<tr>
<td>Langmuir</td>
<td>bad negative fitting slope</td>
</tr>
<tr>
<td>Freundlich</td>
<td>0.44</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Coefficient of determination ($R^2$) at zeolite dose</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2 mg dm(^{-3})</td>
</tr>
<tr>
<td>Langmuir</td>
<td>0.97</td>
</tr>
<tr>
<td>Freundlich</td>
<td>0.36</td>
</tr>
</tbody>
</table>

Source: own study.

Fig. 1. Percent of nickel (Ni) removal with different initial Ni concentration and different zeolite doses; source: own study.
The capacity \( q_{\text{m}} \) 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]:

\[
R_L = \frac{1}{1 + K_L C_o}
\]

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...
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 of 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.
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


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