Mini-Review:
Removal of Heavy Metal Ions Using Pristine and Functionalized Natural Zeolites

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Abstract: Heavy metal ions have attracted significant concern regarding their toxicity in living organisms. Concurrently, the removal of heavy metals by the adsorption method is also under the spotlight because it is effective, less cost-demanding, and easy to operate. To date, natural zeolites become one of the most used adsorbents for it is low cost, abundant in reserve, and has high selectivity towards heavy metal. Zeolites possess negatively charged three-dimensional frameworks built by SiO₄ and AlO₄ tetrahedra, which are balanced by counter-cations. The cations within zeolite frameworks can be exchanged with the heavy metal cations in an aqueous environment. This review comprehensively reports the adsorption capacity of heavy metal ions using pristine and modified natural zeolite. The important aspects, including the physicochemical properties of pristine and modified natural zeolites, heavy metal ion adsorption isotherms, kinetics, and thermodynamics, are discussed in detail. It is imperative to note that the physicochemical properties of natural zeolites greatly determine the adsorption capability. Furthermore, natural zeolites could be modified with various molecules such as surfactants and polymers to improve the adsorption capacity and adsorb heavy metal anions. Ultimately, this review is concluded with prospects for future improvement.

Keywords: adsorption capacity; adsorption isotherm; adsorption kinetics; heavy metal; zeolite

INTRODUCTION

Environmental pollution is a problem that always appears, even common, in the last decade. This type of pollution can come from anywhere, but the most frequent and dangerous sources of pollution are organic materials and heavy metals from industrial wastewater [1-4]. Heavy metals refer to dense metallic elements with high atomic weights or atomic numbers, such as Cd, Hg, Pb, As, Cu, Cr, Mn, Fe, and Zn, which are toxic at relatively low concentrations [5]. The effect of heavy metal intake on the human body through water is fatal since it will accumulate and may lead to organ failure [1,6]. According to WHO, there are limits to those metals in the drinking water, i.e., Cd(II): 3 μg L⁻¹, As(V): 10 μg L⁻¹, Pb(II): 10 μg L⁻¹, Cr(VI): 50 μg L⁻¹, Mn: 0.4 mg L⁻¹, Cu(II): 2 mg L⁻¹, Fe(III): 2 mg L⁻¹, and Zn(II): 3 mg L⁻¹. Cd(II), As(V), and Cr(VI) are classified as carcinogenic heavy metal ions. Cr is divided into two stable species in nature, Cr(III) and Cr(VI), in which the latter is a far more dangerous species than the former. Even so, the limit of Cr(VI) is higher than Cd(II) and
As(V) because it could still be reduced to Cr(III) as long as its dose is under the limit [5]. Pb(II) can cause loss of intelligence quotient in children, whereas Mn(II) has a quite high dose since it is somewhat elusive whether Mn has an adverse effect on humans, albeit it has harmful effects in rodents and other animals [5]. Unlike other heavy metals, Fe and Zn are essential to our bodies. Nevertheless, several studies show that Zn and Fe are poisonous to animals such as fish, sheep, and even humans when it exceeds the limited dose intake [5,7-10].

Several strategies have been devoted to removing heavy metal ions from the aqueous environment, such as ion exchange, neutralization, chelating agent, reverse osmosis, and adsorption [2,11-14]. All these methods have succeeded in removing heavy metal ions from aqueous solutions through the years and have offered some advantages and disadvantages. Those advantages and disadvantages are the keys for researchers and industries to select the preferred method. Neutralization, chelating agent, and reverse osmosis are better in terms of effectiveness for removing heavy metal ions. Yet, the operational cost is very costly, rendering these methods unlikely to be applied in many industries. Ion exchange and adsorption exhibit a high selectivity to the heavy metal ion and a relatively low operational cost. However, ion-exchange limits metal concentration in a solution, making adsorption generally preferred [2,15].

In the adsorption method, there are many types of adsorbent, including biosorbent [16], activated carbon [17], fly ash [2], clay minerals [18], and zeolite [19-20]. As seen in Fig. 1, these materials are used and proven successful in removing metal ions from an aqueous solution. Biosorbent is a material that utilizes microorganisms, such as algae, bacteria, and fungi, dead or alive, to adsorb pollutants on their cell wall or to detoxify the heavy metal by changing its oxidation number, e.g., Cr(VI) to Cr(III) [16,21-23]. However, biosorbent has a significant drawback since it needs to be in a well-controlled environment, such as pH, temperature, and solution matrix, to perform the adsorption of heavy metal ions [16,21]. Furthermore, the effectiveness of adsorption is limited to low heavy metal concentrations [23]. Activated carbon is a carbon material with a large surface area, great active sites, and a porous structure [17]. Nonetheless, even with great active sites, activated carbon has a little too low adsorption capacity and selectivity toward metal ions [17]. Fly ash is an aluminosilicate-based solid waste from a thermal power plant [2,24]. It is cheap but needs chemical activation to improve its adsorption performance [2].

Fig 1. Adsorbent materials structure: (a) Activated carbon. Adapted with permission from Ref [25], Copyright 2017 Sage; (b) Clay. Adapted with permission from Ref [26], Copyright 2018 SCIRP; (c) Biosorbent. Adapted with permission from Ref [27], Copyright 2017 Frontiers; (d) Fly ash. Adapted with permission from Ref [2], Copyright 2019 Elsevier; (e). Zeolite. Adapted with permission from Ref [28], Copyright 2020 MDPI
Clay mineral is an aluminosilicate-based layered material with an ion exchange capacity and large surface area [14,18]. However, due to its swelling properties, it has limited adsorption capacity and low selectivity to heavy metal ions [14]. Zeolite is a crystalline, aluminosilicate material with uniform distribution of micropores (<2 nm) and a large surface area [29-31]. The microporous and negatively-charged structures render the natural zeolite highly effective and efficient for removing heavy metal ions. Zeolite can be naturally-occurred via a hydrothermal-like reaction in the volcanic area. Natural zeolite is cheap yet still possesses high adsorption capacity. Indonesia has more than 400 million tons of natural zeolite reserves [32-33]. Currently, more than 250 different zeolite frameworks to date, and each of them has been assigned a three-letter code by International Zeolite Association (IZA).

This review comprehensively discussed the characteristics of pristine natural zeolite and its application as an adsorbent for removing heavy metal ions from the aqueous environment. Moreover, several routes for modifying the natural zeolites to improve the adsorption performance and enable the removal of heavy metal anions, e.g., Cr(VI), are also elaborated in detail. The heavy metal ions adsorption discussion covers the isotherm, kinetics, and thermodynamic studies.

CHARACTERISTICS OF NATURAL AND MODIFIED ZEOLITE

Pristine Natural Zeolite

Over 50 types of pristine zeolite have been identified worldwide, commonly found in volcanic rocks. The zeolite structure has a three-dimensional framework consisting of SiO₄ and AlO₄ tetrahedra. The isomorphous substitution of SiO₄ with AlO₄ renders a negative charge on the zeolite framework. Hence, counter-cations are needed, such as alkaline and alkaline earth metals and ammonium, which could be exchanged with the other heavy metal ion solution because those cations are weakly held [34]. These pristine zeolites have a unique framework and structure that are relevant to their adsorption and ion exchange capacities. Moreover, pristine zeolites also can be used for separation [35] and catalysis [36-41] due to their structural cavities, porous acid sites, and input channels that can establish molecules like water and other organic molecules. According to IZA, there are over 200 types of zeolite frameworks, and each type is divided by a three-letter code [42].

The physicochemical properties of pristine zeolite determine its structural properties, such as Si/Al ratio, mineral composition, exchangeable cation, and surface area. Si/Al ratio is essential because it causes zeolites to have a negative charge that can attract cations. The lower Si/Al ratio is, the higher its negative charge density, making it better in selectivity and attracting the metal cations [37,43-44].

Mineral composition and exchangeable cations are the factors that are often not considered. Different minerals have distinct properties, making some of the zeolites have higher adsorption capacity than others while having the same solution matrix [45]. Exchangeable cations did play significant roles in the adsorption capacity. For example, the more the exchangeable cation, the more heavy metal ions can be exchanged from the polluted solution [46]. Heavy metal ions are regularly in a divalent state, so a divalent ion exchanger, such as Mg(II) and Ca(II), is commonly better than a monovalent ion exchanger, such as NH₄(I), H(I), and K(I). In other cases, the surface area also played a significant role in the adsorption capabilities of the zeolite. The larger the surface area, the more heavy metal ion can be adsorbed, giving the zeolite more immense sorption capabilities [47]. Therefore, the factors governing the adsorption course are complex, and the adsorption results between different reports should be comprehensively considered before comparison.

Clinoptilolite is one of the most abundant natural zeolites and is commonly utilized by researchers [48-51]. The presence of clinoptilolite is distributed worldwide, including south-east Asia, South America, Europe, Australia, and Africa. Aside from clinoptilolite, other natural zeolites are also explored, such as mordenite, chabazite, stilbite, and phillipsite. The type and composition of pristine natural zeolites are summarized in Table 1. As seen, the Si/Al ratio is relatively low, ranging from around 1 to 6, which generates a highly
negative charge. Thus, natural zeolites are balanced by monovalent cations and divalent cations. The cation-exchange capacity (CEC) and the specific surface area are greatly varied due to the difference in crystallinity, impurities, and other variables. It should be noted many natural zeolites are found in low crystallinity.

**Modified Natural Zeolite**

Pristine natural zeolite’s advantages, including abundant reserve, good adsorption, decent cation exchange capacity, and low cost, are still deemed insufficient since the said advantageous properties could be further enhanced. Therefore, researchers have begun modifying pristine zeolites by incorporating acid or base, polymer, and functional groups for the adsorption of heavy metal ions. The modified natural zeolites are also applied in other fields, such as catalysis [56] and the removal of other inorganic pollutants [57-58]. The vast application of the modified pristine natural zeolite does not rule out the possibility that a new or already found modifier for another field is applicable in heavy metal adsorption.

Yousefi et al. [59] analyzed the clinoptilolite modified with Cobalt Hexacyanoferrate nanoparticles to remove Cd(III) ions from an aqueous solution. The result indicated the Cd(III) ions sorption capacity was improved up to two times higher than non-modified clinoptilolite (51 mg g⁻¹).

Meanwhile, Mirbaloochzehi et al. [60] modified the clinoptilolite using a surfactant (Triton X-100) to remove heavy metal cations (i.e., Cu(II), Pb(II), Ni(II), Cd(II), Fe(II), and Zn(II)) from aqueous solution with cation sorption capacity for Pb(II), Cu(II), Cd(II), Ni(II), Zn(II); and Fe(II) was 91.34, 85.71, 78.27, 76.18, 67.41 and 63.45 mg g⁻¹, respectively. Chitosan nanoparticles were also investigated as a modifier to the natural zeolite to improve the sorption capacity of Pb(II) ions [61]. As a result, the adsorption capacity was increased compared to the non-modified zeolite from 43.83 to 49.91%.

Pristine natural zeolite has impurities within its inner architecture, often impeding micropores. Hence, acid or base is added to eliminate other minerals or substances obstructing the pore so that zeolite can adsorb more heavy metal ions. Another challenge is that pristine zeolite carries a negative charge that cannot adsorb heavy metal anions, such as chromate or bichromate. Consequently, surface modification is necessary to equip the natural zeolite with anion adsorption ability. It includes the addition of polymer or functional groups to the surface of zeolites. Table 2 summarizes several modifiers used by the researchers.

### Table 1. Type and the composition of pristine zeolite

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Zeolite type</th>
<th>Si/Al Ratio</th>
<th>Major cation</th>
<th>CEC (meq g⁻¹)</th>
<th>SSA (m² g⁻¹)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brazilian zeolite</td>
<td>Clinoptilite</td>
<td>4.82</td>
<td>-</td>
<td>1.57</td>
<td>59.63</td>
<td>[48]</td>
</tr>
<tr>
<td>Philippine zeolite</td>
<td>Mix of mordenite, clinoptilolite, and chabazite</td>
<td>4.29</td>
<td>Ca; Fe; Mg</td>
<td>-</td>
<td>222.63</td>
<td>[44]</td>
</tr>
<tr>
<td>Indonesian zeolite</td>
<td>Mix of mordenite and clinoptilolite</td>
<td>4.72</td>
<td>K; Ca</td>
<td>43.20</td>
<td>-</td>
<td>[46]</td>
</tr>
<tr>
<td>Indonesian zeolite</td>
<td>Mix of mordenite and clinoptilolite</td>
<td>5.40</td>
<td>K; Na; Ca; Fe</td>
<td>102.80</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Indian zeolite</td>
<td>Stilbite</td>
<td>2.08</td>
<td>Ca; Na</td>
<td>-</td>
<td>-</td>
<td>[49]</td>
</tr>
<tr>
<td>Russian zeolite</td>
<td>Clinoptilolite</td>
<td>5.00–6.00</td>
<td>K; Na</td>
<td>-</td>
<td>-</td>
<td>[50]</td>
</tr>
<tr>
<td>Iranian zeolite</td>
<td>Clinoptilolite</td>
<td>4.87</td>
<td>K</td>
<td>-</td>
<td>60.43</td>
<td>[51]</td>
</tr>
<tr>
<td>Kazakhstan zeolite</td>
<td>-</td>
<td>4.59</td>
<td>Ca; Fe; Mg; K</td>
<td>-</td>
<td>-</td>
<td>[52]</td>
</tr>
<tr>
<td>Jordanian zeolite</td>
<td>Philipsite</td>
<td>2.96</td>
<td>Fe; Mg; Ca</td>
<td>0.70</td>
<td>41.20</td>
<td>[53]</td>
</tr>
<tr>
<td>Serbian zeolite</td>
<td>Clinoptilolite</td>
<td>-</td>
<td>Ca; Mg</td>
<td>1.38</td>
<td>18.00</td>
<td>[54]</td>
</tr>
<tr>
<td>Slovakian zeolite</td>
<td>-</td>
<td>4.95</td>
<td>Ca; Fe</td>
<td>-</td>
<td>-</td>
<td>[55]</td>
</tr>
</tbody>
</table>

Adsorption methods are commonly used by mixing solid adsorbent materials into a heavy metal solution. The
mixture is then stirred to maximize the adsorption by using a shaker. Then the mixture is separated using centrifugation and screening to free the supernatant from the adsorbent. Afterward, the supernatant is measured, usually by using atomic absorption spectroscopy (AAS) or atomic emission spectroscopy (AES), to determine the number of heavy metal ions that have been absorbed. From these steps, adsorption performance, such as adsorption capacity, isotherm, kinetics, and thermodynamics, can be determined for modeling the adsorption course of adsorption.

### Adsorption Capacity of Pristine Zeolite

Budianta et al. [46] used two Indonesian natural zeolites from Bantengwareng and Tegalrejo, named B and T, respectively, with mordenite types of zeolite and other mineral impurities, for Pb(II) and Cd(II) ion removal. The adsorption capacities of zeolite in B and T for Pb(II) adsorption are 416.67 and 384.61 mg g−1, respectively. Besides, the adsorption capacity is 277.77 and 243.91 mg g−1 for Cd(II) removal of B and T samples. It was shown that the adsorption capacity of B is higher than T regarding the more abundant smectite presence. Hence, B has a higher CEC and SSA compared to T.

Previously, Zanin et al. [48] reported Brazilian zeolite, clinoptilolite type, to adsorb Cu(II), Fe(III), and Cr(III), rendering the adsorption capacity of 1.845, 1.750, and 1.661 mg g−1. The results showed that iron is preferentially to adsorb at the process, which exhibited the selectivity of zeolite to metals. Another natural zeolite, i.e., Slovakian zeolite, is reported by Kovacova and Pla [55], that used successfully to adsorb Ni(II) ion without pre-treatment and achieved an adsorption capacity of 17.62 mg g−1. The sorption process was on the heterogeneous surface with a concentration of nickel solution 50 mg L−1. The Philippine natural zeolite (PNZ), a mixture of mordenite, clinoptilolite, and chabazite, was used for Zn(II) ion removal in an aqueous solution by Gili et al. [44]. The PNZ has rough and corrugated surfaces, high surface area, and contains natural cations, i.e., Fe, which already filled in the zeolite active sites. Hence, it increases the ability to exchange cations, rendering the adsorption capacity of 3.8 mg g−1.

Abd El-Azim and El-Adzim [71] have investigated the clinoptilolite zeolite for Cd(II), Fe(III), and Ni(II) ion removal without pretreating the zeolite. The result exhibited the effectiveness of clinoptilolite, which rendered the adsorption capacity 10.000, 9.971, and 9.901 mg g−1 for Cd(II), Fe(III), and Ni(II), respectively. From these results, it is shown that each metal has

### Table 2. Modifier, textural properties, and cation exchange capacity (CEC)

<table>
<thead>
<tr>
<th>Zeolite type</th>
<th>Modifier</th>
<th>SSA before modification (m² m⁻¹)</th>
<th>SSA after modification (m² g⁻¹)</th>
<th>CEC (meq g⁻¹)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iranian zeolite</td>
<td>Cobalt hexacyanoferrate</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[59]</td>
</tr>
<tr>
<td>Iranian zeolite</td>
<td>Triton x-100 (surfactant)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[60]</td>
</tr>
<tr>
<td>Indonesian zeolite</td>
<td>Chitosan</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[61]</td>
</tr>
<tr>
<td>Iranian zeolite</td>
<td>HDTMA</td>
<td>14.85</td>
<td>9.55</td>
<td>-</td>
<td>[62]</td>
</tr>
<tr>
<td>Mexican zeolite</td>
<td>(Hexadecyltrimethylammonium)</td>
<td>7.73</td>
<td>5.41</td>
<td>-</td>
<td>[63]</td>
</tr>
<tr>
<td>Taiwan zeolite</td>
<td>Alginate Composite</td>
<td>746.00</td>
<td>22.90</td>
<td>1.50</td>
<td>[64]</td>
</tr>
<tr>
<td>Serbian zeolite</td>
<td>HDTMA and dithizone</td>
<td>23.19</td>
<td>HDTMA+ dithizone:</td>
<td>-</td>
<td>[66]</td>
</tr>
<tr>
<td>Mexican clinoptilolite</td>
<td>Metals ion (Fe; Zr; FeZr)</td>
<td>-</td>
<td>-</td>
<td>1.60 ± 0.09</td>
<td>[68]</td>
</tr>
<tr>
<td>Mexican mordenite</td>
<td>Metals ion (Fe; Zr; FeZr)</td>
<td>-</td>
<td>-</td>
<td>1.80 ± 0.06</td>
<td>[68]</td>
</tr>
<tr>
<td>Mexican chabazite</td>
<td>Metals ion (Fe; Zr; FeZr)</td>
<td>-</td>
<td>-</td>
<td>2.10 ± 0.05</td>
<td>[69]</td>
</tr>
<tr>
<td>Slovakian clinoptilolite</td>
<td>NaCl sonication</td>
<td>31.14</td>
<td>37.25</td>
<td>1.58</td>
<td>[69]</td>
</tr>
<tr>
<td>Iranian clinoptilolite</td>
<td>Glycine</td>
<td>97.00</td>
<td>41.14</td>
<td>-</td>
<td>[70]</td>
</tr>
</tbody>
</table>
unique properties which affect the adsorption capacity of zeolite. Moreover, clinoptilolite has higher selectivity to Cd compared to other heavy metals. Liu et al. [72] also used clinoptilolite type zeolite for heavy metals removal, i.e., Pb(II), Zn(II), Cd(II), and Cu(II), as depicted in Fig. 2(a). The desorption capacity of Na(I) does not show the distinct difference between Zn-, Cd-, and Cu-Na exchange. In contrast, the Pb-Na exchange exhibits a much larger desorption capacity (Fig. 2(b)). It is because the quantum fluctuation of Pb(II) renders the strong polarization occurs. Therefore, Pb(II) can exchange more Na(I).

Belova [50] reported a mix of mordenite and clinoptilolite-type Russian zeolite to adsorb Cu(II), Ni(II), Co(II), and Fe(II). The adsorption capacity of Russian zeolite is increasing as follows Cu(II) > Fe(II) > Ni(II) > Co(II). Jorfi et al. [51] used clinoptilolite type Iranian zeolite for the adsorption of Cr(VI) and rendering the adsorption capacity of 2.69 mg g⁻¹. Mihajlović et al. [54] used clinoptilolite to determine its adsorption capacity for Pb(II), Cd(II), and Zn(II) ions. The adsorption capacity is increasing as follows Pb(II) > Zn(II) > Cd(II). Obaid et al. [49] investigated three types of Indian zeolite, which are Mordenite, Stilbite, and Heulandite, to determine the adsorption capacity for Co(II), Zn(II), and Mn(II). The adsorption capacity achieved is Co(II) > Zn(II) > Mn(II). Moreover, mordenite exhibited higher extraction efficiency than Stilbite and Heulandite. It is noted that the extraction of heavy metal is affected by the ion exchange and adsorption processes [49].

Adsorption Capacity of Modified Natural Zeolite

Kragović et al. [65] reported the alginate composite to modify clinoptilolite type zeolite for the adsorption of Pb(II). The adsorption capacity increased from 66 to 102 mg g⁻¹. Hence it can conclude that the increase in sorption intake because of the encapsulation is proven to change the CEC of each cation while did not significantly impact the total CEC of the zeolite. The CEC decreased from 0.23 to 0.15 for Na(I), 0.15 to 0.11 for K(I), and 0.22 to 0.1 for Mg(II). Meanwhile, CEC for Ca(II) is increased from 0.85 to 1.12, making the ion exchange of the zeolite more preferable because of the same oxidation number of the heavy metals and the exchangeable cation. Shirzadi and Nezamzadeh-Ejhieh [66] investigated an Iranian clinoptilolite zeolite modified by two times using HDTMABr (hexadecyltrimethylammonium bromide) and dithizone (DT) to improve its removal ability of the metal ions by adding a complexation process on top of exchanging cation process. The modified zeolite shows higher removal efficiencies for Hg(II) and Pb(II) due to another phenomenon process besides ion exchange, i.e., the process of removing the cations, regarding the complexation process of the cations with free electron pairs of sulfur or nitrogen atoms in DT. Yulizar et al. [61] have modified natural zeolite with chitosan to improve its adsorption capacity by adding a functionalized group. The modified zeolite shows a material in nano-size scale rendering better adsorption ability with an adsorption percentage of 99.68%. Retnaningrum and Wilopo [67]
used natural zeolite modified as bacterial support materials to reduce sulfate and manganese from synthetic wastewater. The study reported the efficiency of manganese and sulfate removal was up to 23% and 15.4%, respectively.

Triton X-100 modified clinoptilolite type zeolite was investigated by Mirbaloochzehi et al. [60] for the adsorption of several ions, such as Pb(II), Cu(II), Cd(II), Ni(II), Zn(II), and Fe(II) and rendering the adsorption capacity of 91.34; 85.71; 78.2; 76.18; 67.41 and 63.45 mg g$^{-1}$, respectively. It showed that the adsorption capacity using Triton X-100 to modify clinoptilolite increased approximately 60–90% more than the unmodified clinoptilolite. Nasiri-Ardali and Nezamzadeh-Ejhieh [70] pointed out the glycine-modified zeolite to adsorption of Pb(II). The zeolite is divided into two powders of nano-sized particles and micro-sized particles named NCP and MCP and then modified by glycine. The glycine is attached to the surface of the zeolite through an ion exchange process with cation from zeolite. Then when the modified NCP and MCP are mixed with heavy metal, ion exchange occurs. The glycine located on the surface of the zeolite is making a complexion process for the heavy metal ion. The complexion process can be done because there is an amino and carboxylic group in the glycine. Hence, the adsorption capacity of MCP and NCP increased from 87.10 to 123.20 mg g$^{-1}$ and 96.71 to 183.15 mg g$^{-1}$.

Nguyen et al. [69] described the sonication and NaCl solution to modify Slovakian clinoptilolite type zeolite to improve its adsorption capacity for Cd(II) ion removal, and this process is called a sonochemical modification. The processes are proven to enhance the natural zeolite’s CEC and SSA. Additionally, the sonochemical process significantly reduces the zeolite’s particle size and size distribution. Hence, the adsorption capacity of modified zeolite increases from 17.63 to 21.47 mg g$^{-1}$. Velazquez-Peña et al. [68] used metal ions, Zr(II), Fe(II), and a combination of both, resulting in a new species of zirconium-iron (FeZr) to modify three types of Mexican zeolite for As(V) adsorption. Those metals ion is used for performing complex with arsenic species. The zirconium-modified zeolite is more efficient than iron-modified zeolite due to the higher affinity of arsenic for zirconium than iron. The adsorption capacity of modified zeolite of Fe(II), Zr(II), and Zr-Fe for clinoptilolite is 0.025, 0.069, and 0.069, respectively. For mordenite, the adsorption capacities are 0.029, 0.079, and 0.072. And for chabazite, the adsorption capacities are 0.05, 0.089, and 0.121 mg g$^{-1}$.

Yousefi et al. [59] have modified clinoptilolite type zeolite with cobalt Hexacyanoferrate (CoHCF) to find a cheaper adsorbent than activated carbon for the adsorption of Cd(II) ion. CoHCF is a complexing agent, allowing the zeolite to remove metal ions from the solution aside from ion exchange. The modification turned out victorious with an adsorption capacity of 51 mg g$^{-1}$, twice the amount of adsorption capacity from the unmodified zeolite. Puspitasari et al. [20] used amidoxime to functionalize Indonesian clinoptilolite type zeolite to increase adsorption capacity toward Pb(II) ion. The adsorption capacity of the zeolite is increased from 52 to 72 mg g$^{-1}$ compared to the initial zeolite. It is due to the chelating functionality of amidoxime groups that adds another prowess to the zeolite, other than ion exchange, to remove the Pb(II) ion. The kinetic study showed that the adsorption rate onto the amidoxime-functionalized zeolite was faster than the initial zeolite. Notably, the adsorption process followed the Langmuir method, and the adsorption kinetics is based on a pseudo-second-order model. Its added prowess proved successful because the zeolite’s adsorption capacity was increased.

HDTMA is one of the most used and effective surfactants to modify zeolite to improve its adsorption capacities toward anion metal ions [62-64]. Several studies show that the HDTMA is attached to the surface of zeolite, therefore decreasing the SSA of zeolite. Despite having a decrease in SSA, it appears that HDTMA brings a positive charge into the surface of zeolite, hence making it can adsorb anion metal [62-64]. Dimas Rivera et al. [63] used clinoptilolite type zeolite to be modified by the HDTMA to adsorb Cr(VI) anion (Fig. 3). Clinoptilolite and clinoptilolite modified exhibited an isotherm type IV and flake-shape particles morphology (Fig. 3(a) and 3(b)). The adsorption
isotherms reveal multilayer adsorption regarding a better adjustment to the Freundlich model for clinoptilolite modified ($R^2 = 0.993$) (Fig 3(c)). The kinetic studies show a better fitting to pseudo-second-order and increased adsorption capacity up to 9.83 mg g$^{-1}$ (Fig. 3(d)). HDTMA created the positive exchange sites to the zeolite surface, and chromate anions occur mainly by interacting with the HDTMA.

Zekavat et al. [62] used clinoptilolite type zeolite to be modified by the HDTMA to adsorb Cu(II) cation and Cr(VI) anion. The studies reveal that the zeta potential of zeolite surface changes from negative to positive charge, making adsorption on anionic metal easily occur. However, the modified zeolite is still deemed capable of adsorption Cu(II) cation with an adsorption capacity of 16.98 mg g$^{-1}$. Thus the sorption of Cu(II) cation on the zeolite improves the intake of Cr(VI) anion because it increases the positive sites on the zeolite. The adsorption capacity for Cr(VI) anion is 27.36 mg g$^{-1}$. Tran et al. [64] reported HDTMA to improve zeolite capability for adsorbing both anion and cation from solution by making a bilayer on the outside surface area, charge in its inner pore. The modified zeolite was then thus making it have a positive charge while having a negative test for adsorption of Pb(II), Cu(II), and Ni(II) cation, as well as Cr(VI) anion. Adsorption capacities of cationic metal are decreased when comparing the HDTMA-modified zeolite to non-modified zeolite. The adsorption capacities for Pb(II) cation are reduced from 159 to 69, 60.1 to 25.6 mg g$^{-1}$ for Cu(II) cation, and 44 to

Fig 3. (a). Nitrogen adsorption-desorption isotherms of clinoptilolite and HDTMA-modified clinoptilolite. (b). SEM images of (i) clinoptilolite and (ii) clinoptilolite modified. (c). Adsorption model for (i) clinoptilolite modified and (ii) clinoptilolite. (d). Pseudo-first order and pseudo-second order for (i) clinoptilolite modified and (ii) clinoptilolite. Adapted with permission from ref [63], Copyright 2021 Elsevier

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22.6 mg g\(^{-1}\) for Ni(II) cation. However, the adsorption capacity of the Cr(VI) anion is increased from 22.9 to 40.5 mg g\(^{-1}\). This result agrees with Zekavat et al. [62], in which the surface of the zeolite changes from a negative charge to a positive charge. It makes the zeolite have a repulsion force for the cation and an attraction force for the anion, resulting in better anion adsorption capacity than cation adsorption capacity.

### ADSORPTION KINETIC, THERMODYNAMIC, AND ISOTHERM

As stated before, the determination of adsorption kinetic, thermodynamic, and isotherm is used for modeling the adsorption processes of the zeolite. Adsorption isotherm is used to determine the interactions between adsorbate and adsorbent, as well as adsorbent characteristics [73]. Some mathematical models can determine the adsorption isotherms, viz Langmuir and Freundlich and also Temkin and Dubin. The derivation of the Langmuir isotherms can be seen in several equations below. Suppose the adsorption process takes place according to Eq. (1) below,

\[
[A] + [S]_{(1-\theta)} \rightleftharpoons [AS]_{\theta}
\]

where [A] is the adsorbate, [S] is a nonbonding surface (1–θ), while [AS] is a bonding surface (θ),

\[V_a = K_a[A]_{(1-\theta)}\]

\[V_d = kd\theta\]

\[V_s\] is the rate of adsorption, and \(V_d\) is the desorption rate. Therefore during equilibrium, we can write Eqs. (4-11) as follow:

\[V_a = V_d\]

\[K_a[A]_{(1-\theta)} = kd\theta\]

\[\theta = \frac{K_a[A]}{K_d}\]

\[0 = K_a[A]_{(1-\theta)}\]

\[0 = K_a[A] - K_a[A]_{(1-\theta)}\]

\[0 + K_a[A]_{(1-\theta)} = K_a[A]\]

\[\theta = \frac{K_a[A]}{a + K_a[A]}\]

Finally, Eq. (11) could be rewritten into Eq. (12) for the adsorption within aqueous solution as follows.

\[
Q_e = \frac{Q_{max}K_L C_e}{1 + K_L C_e}
\]

where \(C_e\) is the concentration of adsorbate at equilibrium, \(Q_e\) is the amount of adsorbate per unit of adsorbent mass in equilibrium, \(Q_{max}\) is the maximum saturated monolayer adsorption capacity of the adsorbent, and \(K_L\) is the Langmuir constant for the affinity between adsorbent and adsorbate. The equation for Freundlich is given in Eq. (13) as follows.

\[
\log Q_e = \log K_f + \frac{1}{n} \log C_e
\]

\(K_f\) is the Freundlich isotherm constant, and \(n\) values vary from zero to one to show the adsorption’s surface heterogeneity or intensity. Nevertheless, if the \(n\) values are unlimited, the Freundlich equation is the same as the Langmuir equation. The Langmuir model is to determine the adsorption characteristic of the sorbent surface as a monolayer. Therefore, the adsorption processes are happening on the surface at each zeolite pore through ion exchange. While the Freundlich model is used to determine the adsorption characteristic of the sorbent surface is heterogeneous. Therefore, the adsorption processes were more than ion exchange, like complexation and sorption at the bilayer of the surface of the zeolite [53,55,64,73-74].

Thermodynamic studies are used to predict the adsorption mechanisms from physical and chemical aspects [75]. The Gibbs energy change (\(\Delta G^o\)) can be calculated by using Eq. (14):

\[
\Delta G^o = -RT \ln K_C
\]

Meanwhile, the thermodynamic parameters can be checked by using the equation that describes the relationship of \(\Delta G^o\), the enthalpy change (\(\Delta H^o\)), and the entropy change (\(\Delta S^o\)) can be written in Eq. (15) as follows:

\[
\Delta G^o = \Delta H^o - T\Delta S
\]

From the equation above, it can be substituted by Van’t Hoff equation, and we can calculate the \(\Delta H^o\) and \(\Delta S^o\) from the slope and intercept in the plot of \(\ln K_C\) versus 1/T using Eq. (16) as follows:

\[
\ln K_C = -\frac{\Delta H^o}{R} \times \frac{1}{T} + \frac{\Delta S^o}{R}
\]

\(R\) is the universal gas constant (8.3144 J mol\(^{-1}\).K\(^{-1}\)), and \(T\) is the temperature (K).

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Adsorption kinetics is used to determine the diffusion of adsorbate in the adsorbent pores and to determine the adsorption uptake at a particular concentration or pressure within a specific time [73]. The two most used for adsorption to determine the adsorption kinetic are pseudo-first-order and pseudo-second-order. The equations for pseudo-first-order and pseudo-second-order are expressed in Eqs. (17) and (18) as follows:

$$\frac{dq_t}{dt} = k_{ad} (Qe - Qt)$$  \hspace{1cm} (17)

$$\frac{dq_t}{dt} = k_{ad} (Qe - Qt)^2$$  \hspace{1cm} (18)

whereas $k_{ad}$ is the adsorption kinetics constant, $Qe$ and $Qt$ are adsorption capacities at equilibrium and at a particular time. The pseudo-first-order indicates that the rate change of adsorbate adsorption over time is directly proportional to the difference in the saturation concentration and the amount of solid adsorption with time or is called physisorption, while the pseudo-second-order indicates the rate of amount adsorbate that has been adsorbed by the adsorbent or commonly called as chemisorption [19,48].

**Adsorption Kinetic, Thermodynamic, and Isotherm of Pristine Zeolite**

For the adsorption kinetics, Gili et al. [44] used intraparticle diffusion, pseudo-first-order, and pseudo-second-order to describe the adsorption kinetics of Ni(II) ion adsorption using mixed zeolite from the Philippines. As seen in Fig. 4, all three models had linear regression ($R^2$) of the curve < 0.90. However, the pseudo-second-order has the biggest $R^2$ at 0.89; thus, the adsorption kinetics followed the pseudo-second-order equation. This work describes the linear function of the kinetic rule to determine the adsorption kinetics.

Zanin et al. [48] pointed out the non-linear pseudo-first-order and pseudo-second-order rules to determine the adsorption kinetics of the three metal ions. The non-linear form for the adsorption kinetics was chosen because it is fitted better than the linear form. For the pseudo-second-order, all metal ions adsorption shows $R^2 > 0.90$, while for the pseudo-first-order, the $R^2$ for Fe(III) ion is 0.85 while both Cu(II) and Cr(III) ion $R^2 > 0.95$. Therefore, for Fe(III) ion adsorption,

![Fig 4. Best fit lines for the linearized kinetic data according to (a) pseudo-first-order, (b) pseudo-second-order and (c) intra-particle diffusion kinetic models; and (d) the resulting plots of each model in comparison to the kinetic data. Adapted with permission from Ref [44], Copyright 2017 IOP Publishing](image-url)
the adsorption kinetics was best described in pseudo-second-order, while for Cu(II) and Cr(III) ion adsorption, the adsorption kinetics was best described in pseudo-first-order. Hence, it can be concluded that pseudo-second-order dominates the kinetic rules for pseudo-second-order, and chemisorption is more dominant in the pristine zeolite. It shows that the interaction between sorbent and sorbate in pristine zeolite indicates ion exchange between metal ions and substitute metal in the sorbent.

Zanin et al. [48] used Freundlich and Langmuir model for all three metals’ adsorption. For Cu(II) ion adsorption for the determination of the adsorption isotherm. It is worth noting that the Langmuir model was not possible because the error is significant. Hence it makes the Freundlich model the best fitted for copper ion adsorption. The two models provide similar $R^2$ for chromium adsorption, 0.96 for Langmuir and 0.93 for Freundlich.

Nevertheless, because Langmuir $R^2$ is higher than Freundlich, the Cr(III) ion adsorption isotherm, best followed the Langmuir model. Lastly, for Fe(III) ion, the $R^2$ was also similar between the two models, 0.98 for Freundlich and 0.95 for Langmuir. For the same reason as Cr(III) ion adsorption, the Freundlich model was chosen for adsorption isotherm of iron(III) ion adsorption because $R^2$ is higher than the Langmuir. In agreement with Zanin et al. [48], Gili et al. [44] used both Langmuir and Freundlich models. The $R^2$ value from the Langmuir model was higher (0.99) than the $R^2$ value of Freundlich (0.97). Therefore, using Philippine zeolites, the Langmuir model was chosen to represent the adsorption isotherm of nickel(II) ion adsorption.

The adsorption of Pb(II) ion using Kazakhstani zeolite shows that the Freundlich model gives an $R^2 < 0.900$ while the Langmuir model gives an $R^2$ value of 0.999 [52]. Therefore, the Langmuir model was the most fitted for its adsorption isotherm. The adsorption isotherm of Cd(II) ion adsorption using phillipsite type zeolite shows that using the Freundlich model, the $R^2$ achieved was 0.80, while for the Langmuir model, the $R^2$ achieved was 0.94 [53]. The data shows that the Langmuir model was best fitted for the zeolite adsorption isotherm.

Abd El-Azim and Mourad [71] used both Langmuir and Freundlich models to describe the adsorption isotherm for its three metal ion adsorption. It is shown that the Langmuir model has $R^2 > 0.99$ for all of its metal ion adsorptions. Freundlich model also gave $R^2 > 0.99$ for Fe(II) and Ni(II) ion. For Cd(II) ion, the $R^2$ value is 0.69, which indicates that for Cd(II) ion adsorption, only the Langmuir model was best fitted for its adsorption isotherm, whereas for Fe(II) and Ni(II) ion, both Langmuir and Freundlich model was best described the adsorption isotherm.

Kovacova and Pla [55] reported both Freundlich and Langmuir models to find its adsorption isotherm for its Ni(II) ion adsorption. Langmuir and Freundlich’s model gives $R^2 < 0.90$, which is relatively low. But, $R^2$ for Freundlich is higher (0.83) than the Langmuir (0.73). Therefore, in this work, the Freundlich model is better to describe the adsorption isotherm than the Langmuir model. The determination of the adsorption isotherm of Cu(II), Co(II), Ni(II), and Fe(II) ion adsorption was conducted using Langmuir and Freundlich model [50]. All four metal ions had $R^2 > 0.95$ using the Langmuir model, while the Freundlich model only gives Fe(II) and Ni(II) ions that had $R^2 > 0.95$ and $R^2 < 0.90$ for Cu(II) and Co(II). Thus, the Langmuir model was chosen for all four metal adsorption isotherms. Mihajlović et al. [54] used three modelings, Freundlich, Langmuir, and Dubinin-Radushkevich, to determine the adsorption isotherm for Pb(II), Zn(II), and Cd(II) ion adsorption. The result exhibited the Langmuir model as an adsorption isotherm for all three metal ion adsorption because, between the three models, Langmuir had the highest $R^2$ or closest to 1.

While using two or more models to determine the adsorption isotherm is common, Budianta et al. [46] and Liu et al. [72] only used the Langmuir model to determine the adsorption isotherm. Budianta et al. [46] use the Langmuir model to determine the adsorption isotherm of the two zeolite samples from B and T for Pb(II) and Cd(II) metal ions. The result shows that using the Langmuir model, the $R^2$ for all adsorption batches is $> 0.800$. Therefore, the Langmuir model is fitted for explaining the adsorption isotherm. The difference in
the $Q_{\text{max}}$ of both zeolites for two cations can be explained because B samples have higher CEC than T samples. Hence making the B samples have higher $Q_{\text{max}}$ than the T samples. Liu et al. [72] used the Langmuir model to describe the adsorption isotherm of Pb(II), Zn(II), Cd(II), and Cu(II). All data show $R^2 > 0.90$. Hence the Langmuir model effectively depicts the adsorption isotherm.

**Adsorption Kinetic, Thermodynamic, and Isotherm of Modified Natural Zeolite**

The pseudo-second-order and the Langmuir model are dominant for pristine zeolite because the ion exchange situation in the pristine zeolite is mostly occurring. However, in modified natural zeolite, the kinetic and isotherm will vary with the addition of a modifier. Kragović et al. [65] used Freundlich and Langmuir model to describe the adsorption isotherm of zeolite-modified alginate for Pb(II) ion adsorption. From the model, Freundlich has a higher $R^2$ (0.96) than the $R^2$ (0.85) of the Langmuir model. Therefore, the adsorption isotherm was determined by Freundlich. It shows that the modifier successfully modifies the zeolite, making the adsorption processes not limited to monolayer, which is correlated with the Langmuir model and has a complex mechanism and heterogeneous surface, which is correlated with the Freundlich model.

Mirbaloochzehi et al. [60] reported the Langmuir and Freundlich model to find the best fit for the adsorption isotherm of surfactant-modified zeolite for the adsorption of Pb(II), Cu(II), Cd(II), Ni(II), and Zn(II).

The $R^2$ value of both models was more than 0.98, thus making the adsorption isotherm fit both Langmuir and Freundlich models. It explained that some of the metal ions that got adsorbed by the surfactant and complexation method, not only in the surface of the zeolite, thus making the modification successful.

Nasiri-Ardali and Nezamzadeh-Ejhieh [70] investigated six different models to determine the adsorption isotherm, which are Dubinin-Radushkevich, Langmuir, Freundlich, Temkin, Redlich-Peterson and Toth model. Among these six models, Langmuir is the best fit for the adsorption isotherm of Pb(II) ion adsorption, with an $R^2$ value of 0.99, as seen in Fig. 5. Adsorption kinetics were studied using both the pseudo-first order and pseudo-second order. With an $R^2$ value of 0.99, the adsorption kinetics follows pseudo-second-order rules. In the adsorption thermodynamics, $\Delta G$ of the adsorption is negative, which means the reaction is performed spontaneously. $\Delta H$ of the adsorption is also negative, meaning the adsorption process is exothermic.

Nguyen et al. [69] reported three adsorption kinetics models to determine the adsorption’s fittest: pseudo-first-order, pseudo-second-order, and Elovich. According to the $R^2$ value, the adsorption kinetics is best fitted for the pseudo-second-order rule. For adsorption isotherm, Langmuir, Freundlich, and Temkin models were used. The three models had an $R^2$ value higher than 0.9, making the three models can be fit to the adsorption isotherm. However, the Langmuir model was identical to the experimental. Therefore, the adsorption isotherm

**Fig 5.** (a) Dubinin-Radushkevich and (b) Langmuir (Freundlich, inset) isotherms for Pb (II) removal by NCP-Gly, (CPb (II): 80, 100, 500, 800, 1000, 2000, 8000, g L$^{-1}$, sorbent dosage: 0.15 g L$^{-1}$, agitation time: 4 h, pH 4). Adapted with permission from Ref [70], Copyright 2020 Elsevier
is followed the Langmuir model. The adsorption thermodynamics show that $\Delta G$ is negative while $\Delta H$ and $\Delta S$ are positive. It showed that the adsorption is spontaneous (from $\Delta G$), endothermic (from $\Delta H$), and increased randomness at the solid/solution interface.

Velazquez-Peña et al. [68] employed Langmuir, Freundlich, and Dubinin-Radushkevich to determine the adsorption isotherm. Based on the $R^2$ value from the three models, Freundlich had the highest $R^2$ value for each type of modified zeolite. The adsorption kinetics was studied using pseudo-first order, pseudo-second order, Elovich, and intraparticle diffusion. Both pseudo-second-order and intraparticle diffusion are best fitted for the adsorption kinetics. The pseudo-second-order explained the chemisorption mechanism of ion exchange between As(V) ion and FeZr modified zeolite. Meanwhile, intraparticle diffusion has explained the adsorption of As(V) ions through the modified zeolite’s pores, channels, and cages. Yousefi et al. [59] also used Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich to determine the adsorption isotherm. From the $R^2$ value, Langmuir is the highest, making it the most fitted for cadmium ion adsorption using modified zeolite. The pseudo-second-order and pseudo-first-order were conducted to find the adsorption kinetics. With an $R^2$ value of 0.91, the adsorption kinetics follows the pseudo-second-order rule.

Puspitasari et al. [20] reported Langmuir, Freundlich, and Temkin to determine the adsorption isotherm. Interestingly, all three of the model give $R^2 > 0.90$, with Langmuir having the highest $R^2$ with a value of 0.99. Therefore, the Langmuir model was chosen to represent the adsorption isotherm of the modified zeolite. The pseudo-first-order, pseudo-second-order, and intra-particle diffusion are used for adsorption kinetics. Among the three rules, the pseudo-second-order has the highest $R^2$ with a value of 0.99. Hence, making the modified zeolite follow the pseudo-second-order rule.

Dimas Rivera et al. [63] used pseudo-first-order and pseudo-second-order to determine the adsorption kinetics for the Cr(VI) anion with the HDTMA modifier. $R^2$ value suggests that the adsorption kinetics followed the pseudo-second-order rule. Langmuir, Freundlich, Sips, and Dubinin-Radushkevich model was used for adsorption isotherm. Between these four models, the $R^2$ value determined that the Freundlich model was best fitted for the adsorption kinetics of modified clinoptilolite. Zekavat et al. [62] determined the adsorption kinetics of the adsorption of Cu(II) and Cr(VI) ions using pseudo-first order and pseudo-second order rules. $R^2$ value tells that the adsorption kinetics follow pseudo-second-order for both metal adsorptions. The adsorption isotherm was determined using Langmuir, Freundlich, and Dubinin-Radushkevich. According to the $R^2$ value, the highest was the Freundlich model for both metal adsorptions. Tran et al. [64] determined the adsorption isotherm using Langmuir and Freundlich model for each metal ion adsorption. The Langmuir model was best fitted for Pb(II) and Cr(VI) ion adsorption. In comparison, the Freundlich models were best fitted for the adsorption of Cu(II) and Ni(II) ions.

### SUMMARY AND PERSPECTIVES

Due to their physicochemical properties and abundance reserve, the pristine and modified natural zeolites have been widely used as an adsorbent for heavy metals. Clinoptilolite is the most used pristine zeolite by the researcher because it is abundant in nature, easy to find, and has good adsorption capabilities. Furthermore, the structure of clinoptilolite makes it easier to adsorb metal ions than any other type. The three prominent factors that determine the adsorption capabilities of the pristine and modified natural zeolite are the specific surface area (SSA), cation exchange capacity (CEC), and the pre-treatment before use. If one of the factors has been improved, then prosperity will increase. Hence, if all factors are taken into account, then the capabilities of the zeolite will improve multiple times better than if only one factor has been done or improved.

Moreover, for modified natural zeolite, the modifier that is generally used often reduces the SSA of the pristine zeolite. Nevertheless, the adsorption capacity increases because the modifier added another chemical reaction to the zeolite adsorption process. The adsorption kinetics for most of the zeolite adsorption...
Table 4. Summary of adsorption condition

<table>
<thead>
<tr>
<th>Metal Ion</th>
<th>Pb(II)</th>
<th>Zn(II)</th>
<th>Cd(II)</th>
<th>Ni(II)</th>
<th>Cu(II)</th>
<th>Fe(II)</th>
<th>Cr(VI)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration range (mg L⁻¹)</td>
<td>331.20–33120.00</td>
<td>189.40–18940.00</td>
<td>100.00–400.00</td>
<td>50.00–200.00</td>
<td>50.00–200.00</td>
<td>1.00–100.00</td>
<td>100.00–1000.00</td>
</tr>
<tr>
<td>Adsorption capacity (mg g⁻¹)</td>
<td>781.87</td>
<td>232.96</td>
<td>384.61</td>
<td>76.18</td>
<td>85.71</td>
<td>9.97</td>
<td>40.50</td>
</tr>
<tr>
<td>Mass of zeolite used (g)</td>
<td>1.00</td>
<td>1.00</td>
<td>10.00</td>
<td>1.00</td>
<td>1.00</td>
<td>0.25–4.00</td>
<td>0.20</td>
</tr>
<tr>
<td>pH</td>
<td>6</td>
<td>6</td>
<td>2–8</td>
<td>2–8</td>
<td>2–8</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Contact time (h)</td>
<td>48.00</td>
<td>48.00</td>
<td>5.50</td>
<td>0.30–2.00</td>
<td>0.30–2.00</td>
<td>0.08–3.00</td>
<td>48.00</td>
</tr>
<tr>
<td>Zeolite type</td>
<td>Clinoptilolite</td>
<td>Clinoptilolite</td>
<td>Mix Clinoptilolite and mordenite</td>
<td>Cliniclupilolite</td>
<td>Cliniclupilolite</td>
<td>Cliniclupilolite</td>
<td>Cliniclupilolite</td>
</tr>
<tr>
<td>Modifier</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Triton x-100</td>
<td>Triton x-100</td>
<td>-</td>
<td>HDTMA</td>
</tr>
<tr>
<td>References</td>
<td>[14]</td>
<td>[14]</td>
<td>[46]</td>
<td>[60]</td>
<td>[60]</td>
<td>[71]</td>
<td>[64]</td>
</tr>
</tbody>
</table>

*in Cr₂O₇²⁻

processes, pristine and modified alike, follow the pseudo-second-order rule. The Langmuir model dominates isotherm for pristine zeolite. For modified natural zeolite, both Langmuir and Freundlich models are frequently used. The Langmuir model explains that the adsorption happens on the surface of the zeolite pore or monolayer. The Freundlich model explained that the adsorption happens not only on the surface of the zeolite but also on the surface of the modifier attached to the zeolite or bilayer. The adsorption processes of pristine and modified natural zeolite are spontaneous. Some are endothermic, while others are exothermic. Table 4 lists the adsorption capacity of metal ions and their tested condition.

Adsorption using zeolite proved to be successful and effective. Nevertheless, the proficiency of adsorbing metal anions is relatively low. The drawback of structure zeolite makes it hard to attract and adsorb the anionic metal phase. The cationic polymer, other than HDTMA with a high affinity toward negative ions, can be a solution to increase the proficiency of the zeolite to adsorb anionic metal. Encapsulating the zeolite surface using inert metal can improve the zeolite catalyst proficiency. It also has made it possible to increase zeolite selectivity between metal ions using the encapsulating method. The metal needed for encapsulating the zeolite does not have to be inert. The more its affinity toward electrons, the more it can attract the anionic metal in an aqueous solution.

Ultimately, several steps should be noted to obtain the optimal zeolite for adsorption processes. First, zeolite must have been through some pre-treatment before use, e.g., grinding, sieving, and washing using deionized or demineralized water. Second, increase the CEC and SSA by dealumination processes using an acid solution, exposure to excess heat using calcination, or washing using alkaline or alkaline earth metal solution. Third, the use of a modifier that added another chemical reaction that can bind metal ions to the zeolite structure other than ion exchange. In addition, it is imperative to acquire the equipoise from economic and environmental points of view to bring a majestic impact not only for the human being but also for all living organisms.

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**AUTHOR CONTRIBUTIONS**

Khairul Ihsan Solihin and St Mardiana wrote and revised the manuscript, Handajaya Rusli supervised and revised the manuscript, and Grandprix Thomryes Marth Kadja conceived the idea, supervised, and revised the manuscript. All authors agreed to the final version of this manuscript.
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