INDONESIA NATURAL MINERAL FOR HEAVY METAL ADSORPTION: A REVIEW

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Abstract

Indonesia has abundant mineral resources used as natural adsorbent materials for the absorption of heavy metal. Among these are natural zeolites, clay, and ashes. These natural materials showed high performance adsorption capacity with respects to their low cost and high availability. Several research reports had been published for studying the performance of the natural materials as adsorbent of several heavy metals i.e., Hg, Pb, Fe, Cd, Cr, Zn, Ni, and Cu by examining the effect of various factors, including pH, contact time, initial concentration, temperature, and dosage. Furthermore, to determine the adsorption rate, mechanism, and efficiency of natural materials in the removal of toxic metals from aqueous solution, investigations have been made of the parameters of the adsorption isotherms, kinetics, and thermodynamics. The main objective of this article is to provide an overview of the use of some natural materials found in Indonesia, including clay, natural zeolite, fly ash, and bottom ash for use as adsorbents for several types of heavy metals in aqueous solution. These types of natural adsorbents were chosen as their high availability in natural or disposal product and their high performance regarding their heavy metal uptakes. This article review is important in order to capture the current research reported the use Indonesia natural minerals as adsorbent of heavy metals and providing its future research opportunities. Thus, we also emphasize the prospect materials and the future research opportunities for the use of Indonesia's local natural minerals with the utilization of non-conventional modification techniques that can provide added value and improve the performance of these natural materials in removing heavy-metal waste from aqueous solutions.

Keywords: Natural Mineral; Clay; Zeolite; Ash; Adsorption; Heavy Metal.

1. Introduction

Human activities release heavy-metal waste into the environment in many different forms, including the effluents of industrial activity, transportation exhaust, municipal sewage, landfills, mining waste, and electroplating. Heavy metals are harmful to the environment and cause a range of public health problems. Eliminating the heavy-metal content from water is important because these elements are not biodegradable and tend to accumulate in living organisms (bioaccumulation), thereby inducing

various diseases and lethal disorders (Masindi & Muedi, 2018). Some heavy-metal elements, like Hg, Pb, and Cr, are extremely toxic to living organisms. Others, like Fe, Mn, Cu, Zn, Ni, and Co, even though essential for life, when present in amounts that exceed certain limits, can be very harmful (Inglezakis et al., 2003; El-Bahy & El-Bahy, 2016; Badillo-Almaraz et al., 2003).

Table 1 shows a list of some of the technologies commonly used to handle the heavy-metal waste dissolved in water, including chemical precipitation, evaporation, ion exchange, electrochemical treatment, membrane technology, and biological treatment (Masindi & Muedi, 2018; Barakat, 2011). However, these technologies faced many problems as their needs of large-scale application, address high-solute pollutant concentrations and the disposal of their byproducts. The biological treatment as an example, its application faced challenges in terms of expensiveness, in-situ treatment failure, its limitation among several heavy metals, and the need for biological agent disposal. Moreover, the adsorption technology, by contrast, has been applied to deal with inorganic and organic waste and has several significant advantages, including its low cost and being easy to apply, efficient, and effective in comparison to other technologies. The adsorption process involves the presence of a material that acts as an adsorbent of pollutant molecules either through the formation of chemical bonds or via interactions between molecules.

Table 1. Comparison of current technologies used for heavy-metal removal

Type of Technology	Advantages	Disadvantages
Precipitation and Coagulation	Economically feasible, suitable for concentrations higher than 1000 mg/L	Requires a large amount of chemicals, slower removal process, high sludge production, and formation of large particles.
Adsorption	Flexibility and simplicity of design, economically feasible, ease of operation and insensitivity to toxic pollutants	Requires the regeneration of adsorbent materials.
Ion exchange	Good removal of a wide range heavy metal	Adsorbents require regeneration or a disposal process, can't handle concentrated metal solutions, nonselective and highly dependent on pH
Membrane Technology	High rate of removal of heavy metals	Expensive, pores are easily blocked by fouling, high sludge production as insoluble matter.
Biological Treatment	Feasibility in removing some metals	Only feasible for removing some metals. Disposal of biological agent required

(Source: Masindi & Muedi, 2018; Barakat et al. 2011; Ariffin et al. 2017)

Some adsorbent materials that have been commonly used in adsorption technology include synthetic materials such as activated carbon (Nejadshafiee & Islami, 2019), zeolitic synthetic materials, geopolymers (Darmayanti et al., 2019), metal–organic frameworks (MOFs) (Kobielska et al., 2018), MCM-41 (mesoporous silica) (Zhu et al., 2017), and natural materials such as clay, natural zeolite, and bottom ash and fly ash, which are waste materials produced from combustion processes (João et al., 2019; Puspitasari, et al., 2019). Synthetic adsorbent materials require expensive preparation, a manufacturing process involving several chemicals, and long synthesis stages, which make this technology relatively impractical for heavy-waste removal (H, 1999). In contrast, natural adsorbent materials have several advantages, including their abundant availability in nature, ease of preparation, good adsorption properties, and relatively low prices (Hegazi, 2013).

Furthermore, the use of natural mineral as adsorbent materials has been exhibited high performance in terms of their heavy metal uptakes. The several optimum conditions have also reported as their highest performance achieved. Also, the modification using several techniques such as thermal treatment, acid-base activation for adding or opening the active site, utilizing the additional functional groups, and reducing their particle size into nanomaterials scales has also exhibited the increase of their performance.

Indonesia has abundant mineral resources and several of the natural adsorbent materials commonly used in the absorption of heavy-metal waste are available in the regions of Indonesia. Among these are natural zeolites, in which their proven reserves are around 447.490.160 tons. Their resources are distributed throughout several regions in West Java, Central Java, Yogyakarta, Lampung, Banten, East Nusa Tenggara, West Sulawesi, and South Sulawesi (Kusdarto, 2008). In addition, Indonesia has abundant clay reserves. Some of the areas containing clay mineral resources are West Kalimantan, South Kalimantan, and the Bangka and Belitung Islands. Others are spread across the islands of Sumatra, Java, and North Sulawesi (Zainith et al., 2002). Moreover, Indonesia has many of volcanos throughout the islands. Their volcanic materials as natural ashes are available in abundant quantities. Also, Indonesia has high resources of fly ash and bottom ash produced by coal-fired power plant. Yet, the utilization of natural, fly and bottom ashes remains very limited. On the other hand, the high contents of silica, alumina, and calcium oxide within these materials are potential for the use as an adsorbent (Darmayanti et al., 2018).

The main objective of this article is to provide an overview of the use of the natural materials found in Indonesia, including clay, natural zeolite, fly ash, and bottom ash, as adsorbents for several types of heavy metals in aqueous solution. It is important for providing the state of the art of reported works and highlighting the future prospect of Indonesia natural materials as their high availability and their future prospect by using several modification techniques. Within this article, we described some of the adsorption experiment being conducted with respect to their kinetics, isothermal characteristics, and thermodynamics. We also highlighted the properties of adsorbents that are the determining factors in their absorption mechanisms.

2. Methods

This is a review article written through a systematic literature survey regarding the use of natural mineral as adsorbents to remove heavy metal cation pollutants. It should be stressed out that we limit our review within the scope of natural mineral from Indonesia. The review is divided into two main points of results and discussion, i.e. types of natural adsorbent and adsorption performances. The former describes the various Indonesia natural minerals functioning as adsorbents, including natural zeolites, clay, and ash, while the latter elaborates the performances of the said adsorbents.

3. Results and Discussion

3.1 Types of Natural Adsorbents

3.1.1 Natural Zeolites

Natural zeolites are naturally occurring microporous (<2 nm) hydrated aluminosilicate minerals. Most common natural zeolites are formed by the alteration of glass-rich volcanic rocks (tuff) by freshwater in playa lakes or by seawater (Gandy et al., 2015). Many natural zeolites have been identified and are prevalent throughout the world, including clinoptilolite, mordenite, phillipsite, chabazite, stilbite, analcime, and laumontite. Offretite, paulingite, barrerite, and mazzite, are much rarer forms. Among the natural zeolites, clinoptilolite is the most abundant and is used worldwide (Wang & Peng, 2009). Structurally, zeolites consist of three-dimensional frameworks of SiO_4 and AlO_4 tetrahedra. The aluminum ion is small enough to occupy a central position in the tetrahedron of four oxygen atoms, and the isomorphous replacement of Si^{4+} by Al^{3+} produces a negative charge in the lattice. The net negative charge is balanced by the exchangeable cation present (sodium, potassium, or calcium). These cations are exchangeable with certain cations in solution, such as lead, cadmium, zinc, and manganese (Barer, 1987; Breck, 1964). The surfaces of natural zeolites are typically negatively charged and therefore only effective for cation exchange. There are also several limitations in their adsorption due to the small cation radii and lower interaction levels. As such, many researchers are working to improve the capacity and selective adsorption of natural zeolites to overcome their poor adsorption performances.

Table 2. Structural Properties of Natural Zeolite

Zeolite type	Chemical Formula	Structure type
Clinoptilolite	$(K_2, Na_2, Ca)_3 Al_6Si_{30}O_{72} \cdot 21H_2O$	HEU
Mordenite	$(Na_2, Ca)_4 Al_8Si_{40}O_{96} \cdot 28H_2O$	MOR
Phillipsite	$K_2(Ca, Na_2)_2Al_8Si_{10}O_{32} \cdot 12H_2O$	PHI
Chabazite	$(Ca, Na_2, K_2)_2Al_4Si_8O_{24} \cdot 12H_2O$	CHA
Stilbite	$Na_2Ca_4Al_{10} Si_{26}O_{72} \cdot 30H_2O$	STI
Analcime	$Na_{16}Al_{16}Si_{32}O_{96} \cdot 16H_2O$	ANA
Laumontite	$Ca_4Al_8S_{16}O_{48} \cdot 16H_2O$	LAU
Offretite	$(CaKMg)(H_2O)_{16}[Al_5Si_{13}O_{36}]$	OFF
Paulingite	$(Ca_{0.5},K,Na,Ba_{0.5})_{10} (H_2O)_{27-34}[Al_{10}Si_{32}O_{84}]$	PAU
Barrerite	$(Na,K,Ca_{0.5})8(H_2O)_{26} [Al_8Si_{28}O_{72}]$	STI

3.1.2 Clay

As a natural zeolite, clay has been developed as a potentially low-cost material with a high specific surface area, cation-exchange capacity, and chemical and mechanical stability (Tong, et al., 2011). The utilization of clay to remove heavy metals from aqueous solution has been studied and is highly recommended because of its abundance and natural availability, technical and engineering feasibility, and cost effectiveness. Bentonite is a clay material found in many countries around the world (Sprynsky et al., 2006). It is produced from volcanic activity containing montmorillonite, a type 2:1 aluminosilicate mineral (Anirudhan & Suchithra, 2010). Bentonite is made from two Si-tetrahedral sheets and an Al-octahedral sheet (**Figure 1 and 2**). In addition, montmorillonite has an amphoteric pH-dependent surface and a high exchange capacity due to the isomorphous substitution of Al^{3+} for Si^{4+}. This surface provides a suitable adsorption site for cation species and makes it a potential alternative adsorbent for heavy-metal adsorption.

The bentonite deposits in Indonesia are mainly Ca- or Mg-type, which are generally suitable as raw materials for absorbing and whitening soils. In East Java, bentonite reserves are found in several areas, e.g., Pacitan, Ponorogo, Blitar, and Trenggalek, with a total reserve of more than 500 million tons (Koswojo, et al., 2010). Recently, several studies have been conducted on the use of bentonite clay to remove lead (Nathaniel et al., 2011; Soetaredjo et al., 2017), but further research is needed to improve its performance.
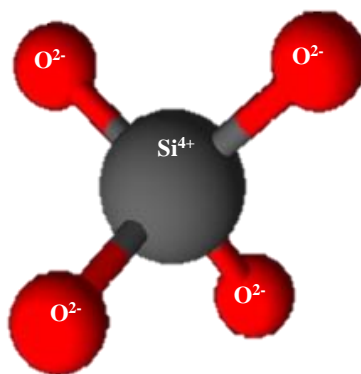
Figure 1. Silica layer consisting of SiO_4^{2-} tetrahedron connected at three corners to form a
hexagonal network
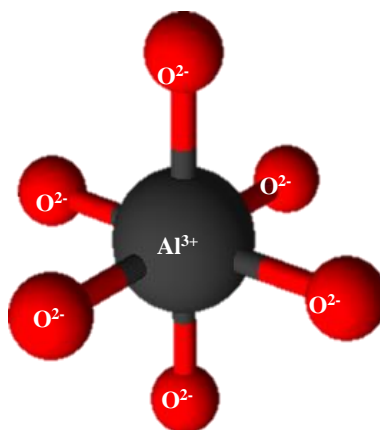(Source: Weaver & Pollard, 1973)

Figure 2. Alumina layer consisting of AlO_6^{4-} octahedron
(Source: Weaver & Pollard, 1973)

3.1.3 Ash

In this article, our ash discussion is focused on types of volcanic ash, fly ash, and bottom ash. First, volcanic ash is produced from the explosion of a volcanic mountain and contains minerals such as iron (Fe), manganese (Mn), silicate (Si), aluminum (Al), calcium (Ca), potassium (K), and phosphor (P). Uniquely, the characteristics of volcanic ash are influenced by the characteristic of the minerals contained in the mountain. Therefore, it has specific properties related to its chemical composition. Volcano ash has potential for use as an adsorbent because it has a high silicate content and is abundantly available. Studying the development of a low-cost ash-based material obtained from mountains as a natural adsorbent remains interesting because each ash is likely different in its capacity to remove heavy-metal ions from water or wastewater. Considering the huge availability of ash after an eruption and its high adsorption capacity, it is urgent that studies be conducted toward the development of alternative adsorbents based on volcanic ash.

Other than volcanic ash, the most common types of ash are fly ash and bottom ash, which are residues from coal combustion. About 80–90% of coal-combustion residues are fly ash and 10–20% are bottom ash (Perera & Trautman, 2006). In 2015, Indonesia alone produced 461 million tons of coal, 87 million of which was approved and provided for domestic supply (Darmayanti et al., 2018).

High volumes of fly ash and bottom ash cause disposal problems. The heavy-metal content of these materials requires special land for their isolation. The main ingredients of fly ash are silica, alumina, iron oxide, calcium oxide, magnesium oxide, and carbon, which are ideal absorbent metals. The potential for using fly ash in wastewater treatment processes is clear because it can be obtained in large quantities at low cost and can be used as both an adsorbent and as a neutralizing agent (Weng & Huang, 2004). Several studies have reported the potential significance of the use of fly ash as an adsorbent for several types of heavy metals. The primary components in bottom ash are generally silica, alumina, iron, and calcium oxide. Other components include magnesium, potassium, barium, potassium, sodium, and titanium oxide in percentages less than 4%, but the number of heavy metals must be considered.

3.2 Adsorption Performances

The adsorption process in a heavy-metal solution had been studied extensively due to its relative advantages over other removal methods. **Figure 3** shows an illustration of the experimental procedure used for heavy-metal removal by adsorption. The adsorption process is conducted by mixing the heavy-metal aqueous solution with adsorbent materials. Due to their reversible characteristics, the adsorbents can also be regenerated by the utilization of a suitable desorption process. During the adsorption process, the parameters that should be considered include the physical and chemical characteristics of the adsorbents and adsorbate, temperature, contact time, pH, and the concentration of the adsorbate in aqueous solution. Generally, there is no general optimum condition that can be applied to all the adsorbent materials. This is because they each have specific properties related to their chemistries and physical compositions.

Sorption isotherms and kinetics are commonly used to describe the interaction mechanism between adsorbate ions and the surface of an adsorbent. The adsorption isotherm models commonly used to analyze the isotherm mechanisms are described using Langmuir and Freundlich models, whereas the kinetics models are typically either pseudo-first order or pseudo-second order. Table 2 shows the adsorption models typically applied to determine the reaction between an adsorbate and adsorbent.
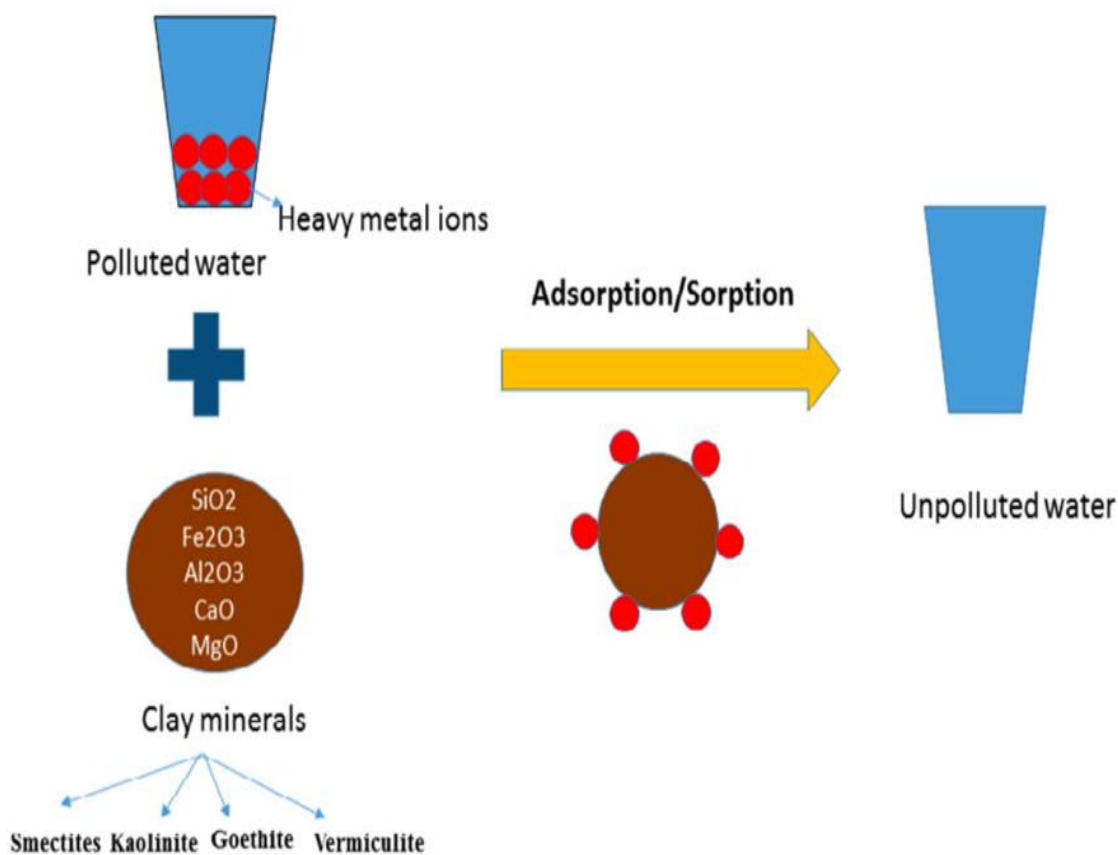
Figure 3. Illustration of heavy-metal-polluted water undergoing an adsorption process with a natural mineral as the adsorbent material

Table 3. Summary of isotherm and kinetics models used to describe the mechanism of adsorption

Isotherm Adsorption Model	Equations	Notes;
Langmuir	$$\frac{Ce}{Qe} = \frac{Ce}{Qm} + \frac{1}{Qm \times K_L}$$	Q_e is amount of adsorbate per unit of adsorbent mass in equilibrium, Ce is concentration of adsorbate at equilibrium, Qm, and K_L are Langmuir constants associated with the adsorption capacity and adsorption rate.
Freundlich	$$\log Q_e = \log K_f + \frac{1}{n} C_e$$	K_f is Freundlich isotherm constant. The n values range from zero to one and reflect the intensity of adsorption or surface heterogeneity

Isotherm Adsorption Model	Equations	Notes;
Temkin	$$Q_e = \frac{RT}{b_T} ln C_e$$	b_T is a constant associated with the heat of the adsorption
Dubinin Radushlecih	$$ln Q_e = ln Q_s - K_{ad} \times \varepsilon^2$$	K_{ad} is an isothermal Dubinin–Radushkevich adsorption equilibrium constant and ε is Dubinin–Radushkevich isothermal constant.

Kinetics Model	Equations	Notes
Pseudo-first order	$$\frac{dq_t}{dt} = K_{ad}(Q_e - Q_t)$$	q_{eq} is the adsorption capacity at equilibrium
Pseudo-second order	$$\frac{dq_t}{dt} = K_{ad}(Q_e - Q_t)^2$$	q_t is the adsorption capacity at time t
		K_{ad} is an adsorption kinetic constant

(Source: Iryani et al. 2018)

3.2.1 Natural Zeolite

3.2.1.1 Natural Form

Some natural zeolites have been used either directly or in pre-treated form after heating, calcination, or soaking in acidic or basic solutions. These treatments are performed in open active sites containing zeolite material to ensure high performance. The use of natural zeolite material as an adsorbent of polluted groundwater was investigated by Pich et al. (2010), using zeolite containing the clinoptilolite and montmorillonite phases originating from Sidomulyo, Gedangsari District, Gunungkidul, Yogyakarta. Adsorption studies were conducted on groundwater containing the metal ions Cd^{2+} (0.01 ppm), Cr^{6+} (0.04 ppm), Cu^{2+} (0.14), Fe^{3+} (0.02 ppm), and Zn^{2+} (0.11 ppm). The results showed that zeolite material can adsorb faster than bentonite, which was used for comparison because of the high cation-exchange capacity of zeolite as compared to bentonite. In addition, this study demonstrated the selectivity of metal ions to adsorption by clinoptilolite and montmorillonite, which was respectively $Cd^{2+} > Cu^{2+} > Cr^{6+} > Zn^{2+}$.

Copper (II) ion adsorption using natural zeolite extracted from Pidie Aceh has shown optimum results with a binding efficiency up to 99.86% and an adsorption capacity of 7.789 mg/g (Yulianis et al., 2017). The zeolite used was ground to nano size to increase the surface area of the zeolite material and open the access to functional groups inside the zeolite. In addition, the activation process used HCl to remove impurities and activate the protonation of active groups on the zeolite surface. The copper (II) ion isothermal adsorption study by Yulianis et al. (2017) used activated natural zeolite and the results revealed that the adsorption characteristics reflected a Freundlich model and the kinetics were pseudo-second order. The results showed that the adsorption occurs on the surface of this heterogeneous adsorbent.

Pratomo et al. (2017) also used natural zeolite as a heavy-metal adsorbent. The natural zeolite was activated by H_3PO_4 and then heated to stretch the inter-porous space to enable the activator to penetrate small pores and force from the pores any impurities and residual organic matter still attached (Anggara et al., 2013). The optimum conditions for the adsorption of Cd (II) metal ions by activated natural zeolites was found to occur within 60 minutes with 2.39 mg/g of Cd (II) metal ions adsorbed at an optimum pH of 5. The study of the kinetics and isothermal adsorption of Cd (II) metal ions by natural and activated zeolites have utilized the Ho kinetics model (pseudo-second order) and Langmuir isotherm model.

Adsorption of iron (III) ions using natural zeolite has also shown good performance (Renni et al., 2018). The natural zeolite is first activated with nitric acid to remove impurities in its framework. The presence of impurities results in less than optimal adsorption of metal ions. The contact time variations show that the longer is the contact time, the less effective are both natural and activated zeolites. The adsorption of zeolite activated on the Fe (III) metal ion follows a Langmuir isotherm pattern with a maximum capacity (Q_m) of 1.18 mg/g.

Iron (III) ion adsorption by sonication treatment was also investigated using natural zeolite from Sumbermanjing Wetan (Alfanaar et al., 2017). The natural zeolite was activated by fluoride acid and hydrochloric acid. The zeolite adsorption kinetics were found to be pseudo-first order, in accordance with the Santosa equation, whereas the isotherm adsorption study reflected a Freundlich model with a non-homogeneous surface and different adsorption capabilities for each molecule. Sonication waves cause uneven collisions on the surface of the adsorbent so that the adsorption ability differs for each molecule and the isotherms becomes Freundlich in nature.

Studies of natural zeolite adsorption on Cr (VI) ions show an interesting phenomenon (Renni et al., 2018). The speciation of Cr (VI) metal ions were found to differ depending on the pH of the solution. At low pH or between pH values of 1–6.5, Cr (VI) ions are in the form of $HCrO_4^-$ or $Cr_2O_7^{2-}$, whereas at high pH or between pH values of 7–10, they are in the form of CrO_4^{2-}. This causes the process of metal-ion adsorption to differ depending on the pH. Cr (VI) adsorption on natural zeolite, as reported by Renni et al. (2017), who used activated natural zeolite in the adsorption process at an optimum pH of 7 with a Freundlich isotherm type and a surface heterogeneity parameter value of 0.17.

The adsorption of lead (II) ion using natural zeolite was reported by Puspitasari et al. (2019). In their study, adsorption was performed using natural zeolites from three regions in Indonesia, i.e., Bayah in Banten, South Lampung, and Nanggung, Bogor. The natural zeolite from Bayah and Lampung predominantly consisted of clinoptilolite frameworks whereas the major phase of Naggung zeolite was mordenite (MOR). The adsorption process of the clinoptilolite frameworks in zeolite demonstrated a higher adsorption capacity than those of modernite due to the compatibility of the lead (II) ions in the pores. In addition, the lower Si/Al ratio of clinoptilolite provides a more negative charge, which attracts more lead (II) ions than mordenite.

South Sulawesi Toraja zeolite has also been reported to be a competitive adsorbent material. The results of adsorption studies on Ni metal ions conducted by Antaria et al. (2018) showed optimum adsorption at a pH of 5.8 with an initial concentration of 5 ppm. Langmuir's adsorption model was found to be appropriate for this adsorption process.

3.2.1.2 Modified Form

Mudasir et al. (2016) modified natural zeolite by coating its surface with dithizone compounds equipped with active -SH and -NH groups to increase their interaction with mercury ions (Hg^{2+}) through covalent interactions. Fourier-transform infrared spectroscopy (FTIR) analysis of the modified zeolite shows a new bond formed between zeolite and dithizone, as indicated by a spectral shift and the emergence of new peaks in dithizone after the immobilization process, as compared to the dithizone prior to its modification of natural zeolite.

A comparison of the adsorption capacities of the zeolite with and without the immobilization of dithizone shows that, in general, the zeolite immobilized by dithizone shows a greater and optimum adsorption capacity at a pH of 6, whereas the optimum for pure natural zeolite occurs at pH 7. The optimum points at pH values of 6 and 7 occur because under acidic conditions, there are active sites in both the adsorbents that are undergoing protonation, whereas, under these conditions, these active sites have already undergone deprotonation and are thus able to form bonds or interact with mercury ions.

The initial concentration effect shows that the optimum concentration for the adsorption process when using dithizone-immobilized zeolite increases from 4 mg/L to 6 mg/L with an optimum adsorption capacity of 1.5 mg/g to 2.5 mg/g. The presence of functional groups in the dithizone-immobilized zeolite is responsible for the increase.

Thermodynamic analysis of the adsorption on natural zeolite either without or with dithizone immobilization shows that the chemical interactions that occur are chemical bonds with an adsorption energy of 36.09 kJ/mol or 39.55 kJ/mol, respectively. The analysis of the optimum adsorption contact time of the non-immobilized natural zeolite was 60 min, whereas on the dithizone-immobilized natural zeolite the optimum contact time was 90 min. Kinetic analysis using the Langmuir–Hinshelwood method showed a higher kinetics constant for the dithizone-immobilized zeolite.

Modification of natural zeolite for its application as an adsorbent material has also been reported by Neolaka et al. (2018). In their study, the authors modified natural zeolite obtained from Ende-Flores as a supporting material for Cr (VI)-imprinted poly (4-VP-co-MMA) (IIP). This modified natural zeolite was used as a Cr (VI) ion adsorbent material, which is a dangerous heavy metal when present in the environment. The optimum conditions for Cr (VI) adsorption on IIP-ANZ and NIP-ANZ were a contact time of 30 min, a pH of 2, and a temperature of 303 K at a 0.1 g adsorbent dose, to yield an adsorption capacity of 4.365 mg/g for IIP-ANZ and 0.107 mg/g for NIP-ANZ at an initial concentration of 14 mg/L. The adsorption process of IIP-ANZ and NIP ANZ occurs at low pH values because under these conditions the chromium species in the solution are in anionic form (CrO_4^{2-} and $Cr_2O_7^{2-}$) and the adsorbent surface is positively charged. Further analysis of the adsorption kinetics of IIP-AN and NIP-ANZ revealed that they follow a pseudo-second-order model. Analysis of the isotherm model of the adsorption of both types of adsorbents conforms to the Langmuir model, whereby the adsorption process occurs on one surface layer of the adsorbent material.

The thermodynamic adsorption study of these two adsorbents showed different characteristics, with the IIP-ANZ adsorption enthalpy being exothermic and the NIP-ANZ adsorption enthalpy being positive or endothermic. But both adsorbents exhibited a negative ΔG value, which indicates spontaneity of the adsorption process. The IIP-ANZ and NIP-ANZ selectivity test results for the adsorption of Cr (IV) ions in the presence of other metals such as Pb (II), Mn (II), Ni (II) and Cr (III) reveal that the adsorption of Cr (IV) on IIP -ANZ has greater affinity than that of other ions. In addition, the selectivity (k') of Cr (IV) adsorption on IIP-ANZ was greater than that on NIP-ANZ for all metal ions.

The performance of modified natural zeolite in the adsorption of heavy metals was also reported by Puspitasari et al. (2018). In their study, the authors prepared modified natural zeolite using a two-step method involving γ-irradiation for the grafting polymerization of polyacrylonitrile (PAN) and chemical transformation of the nitrile groups to amidoxime groups. Amidoxime-functionalized natural zeolite was then used to adsorb the lead (II) ion, and was found to achieve a maximum adsorption capacity of 72 mg/g. This is illustrated in **Figure 4**. This result was very similar to those reported in previous studies of IIP-modified Indonesian natural zeolite, which achieved 4.365 mg/g in optimum conditions (Neolaka et al., 2018). In addition, the adsorption process followed the Langmuir isotherm model with a pseudo-second-order kinetics model.

Thus, the result findings highlighted that both natural and modified zeolites have shown the high adsorption performance for heavy metal uptakes. In which, the non-modified natural zeolites exhibited the adsorption efficiency as 99.86% for Cu^{2+} uptake. In addition, the Amidoxime-functionalized natural zeolite has shown the highest adsorption capacity as 72 mg/g for Pb^{2+} removal. This result indicated the improvement of adsorption performance of natural zeolite due to the modification technique.
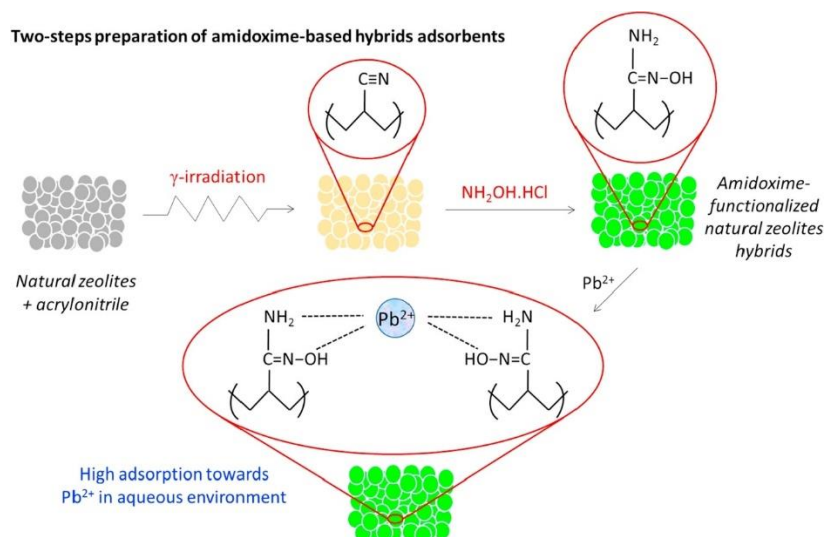
Figure 4. Modification of natural zeolite with poly(amidoxime) for enhanced Pb^{2+} adsorption.

(Source: Puspitasari et al., 2018. Reprinted with permission. Copyright Elsevier.)

Table 4. Adsorption of heavy-metal ions on various Indonesian natural zeolites.

Natural Zeolite Origin	Modificatuon/ treatment	Metal	Adsorption Capacity	References
Gunung Kidul	-	Cd^{2+} Cr^{6+} Cu^{2+} Fe^{3+} Zn^{2+}	$Cd^{2+}> Cu^{2+}>$ $Cr^{6+}> Zn^{2+}$	(Pich et al., 2010)
Pidie, Aceh	-	Cu^{2+}	99.86% and 7.789 mg/g	(Yulianis et al., 2017)
-	H_3PO_4 activated	Cd^{2+}	2.39 mg/g	(Pratomo et al., 2017)
Gunung Kidul	HNO_3	Fe^{3+} Cr^{6+}	36,9% for Fe^{3+} 68,05 for Cr^{6+}	(Renni et al., 2018)
Sumbermanjing Wetan	HF and HCl activated Sonication	Fe^{3+}	-	(Alfanaar et al., 2017)
Toraja	-	Ni^{2+}	-	(Antaria et al., 2018)

Natural Zeolite Origin	Modificatuon/ treatment	Metal	Adsorption Capacity	References
Wonosari	Coated with Dithizone	Hg^{2+}	2.5 mg/g	(Mudasir et al., 2016)
Ende-Flores	imprinted poly (4-VP-co-MMA)	Cr^{6+}	4.365 mg/g	(Neolaka et al, 2018)
South Lampung	Amidoxime-functionalized	Pb^{2+}	72 mg/g	(Puspitasari et al., 2018)
South Lampung, Bayah, Nanggung	-	Pb^{2+}	52 mg/g	(Puspitasari et al., 2019)

Table 5. Isotherms and kinetics of the adsorption of heavy-metal ions on Indonesia natural zeolites

Origin	Modificatuon/ treatment	Metal	Isoterm	Kinetics	References
Gunung Kidul		Cd^{2+} Cr^{6+} Cu^{2+} Fe^{3+} Zn^{2+}	-	-	(Pich et al., 2010)
Pidie, Aceh		Cu^{2+}	Freundlich	Pseudo-Second order	(Yulianis et al., 2017)
-	H_3PO_4 activated	Cd^{2+}	Langmuir	Pseudo-Second order	(Pratomo et al., 2017)
Gunung Kidul	HNO_3	Fe^{3+} Cr^{6+}	Langmuir	-	(Renni et al., 2018)
Sumbermanjing Wetan	HF and HCl activated Sonication	Fe^{3+}	Freundlich	Santosa	(Alfanaar et al., 2017)

Origin	Modificatuon/ treatment	Metal	Isoterm	Kinetics	References
Toraja	-	Ni^{2+}	Langmuir	-	(Antaria et al., 2018)
Wonosari	Coated with Dithizone	Hg^{2+}	Langmuir	Langmuir–Hinshelwood	(Mudasir et al., 2016)
Ende-Flores	imprinted poly (4-VP-co-MMA)	Cr^{6+}	Langmuir	Pseudo-Second order	(Neolaka et al, 2018)
South Lampung	Amidoxime-functionalized	Pb^{2+}	Langmuir	Pseudo-second order	(Puspitasari et al., 2018)
South Lampung, Bayah, Nanggung	-	Pb^{2+}	Langmuir	-	(Puspitasari et al., 2019)

3.2.2 Clay

3.2.2.1 Natural Form

The natural form of clay was used by Pranoto et al. (2018) by physically mixing it with andisol soil to chemically activate it in NaOH solution, followed by washing and drying. The andisol soil was mixed with clay in a range of compositions. Both andisol and clay have several functional groups such as OH, Si-O, and Al-O, as well as components such as kaolinite, gibbsite, feldspar, and allophane. These functional groups are capable of providing an electronegative charge on their surfaces to enable the material to adsorb metal ions in Cd(II) solutions. A 60:40 composition of clay and anisol showed a higher adsorption capacity than other ratios (17.9 mg/g). Although andisol has a greater surface area (257.84 m^2/g) than clay (56.54 m^2/g), its higher acidity (4.18 mmol/g) limits its ability to adsorb the Cd(II) ion. In addition, heat treatment was applied to the adsorbent material to determine its effect on the adsorption capacity. The optimum heat treatment was found to be 100 and 200 °C, which increased the porosity of the adsorbent due to the evaporation of water molecules and the organic content blocking the pores. Higher temperatures may decrease the adsorption capacity of the adsorbent by damaging the adsorbent structure and thereby decreasing the surface area (Henry et al., 2013). Isotherm studies of the adsorption process closely fit the Freundlich model, in which adsorption occurs on one surface with heterogenous and different surface binding energies (Dessalew et al., 2012).

The use of clay as an adsorbent was also reported by Priadi et al. (2014), who used clay containing 28.4% kaolinite ($Al_2(Si_2O5)(OH)_4$) and a predominant quartz content. Their study investigated the adsorption of lead (II) and zinc (II) metal ions with variations in pH. The adsorption of lead by clay was found to be optimum at a pH of 8, although the adsorption results showed the greatest reduction in the amount of Pb at a pH of 12. However, this phenomenon was thought to occur because of the deposition of Pb. The adsorption results for Zn metal showed no significant reduction. The optimum contact time for the adsorption of Zn was determined to be 60 min for a 30% absorption rate, whereas that of Pb was 10 min for 88% absorption. These results indicate significant adsorption efficiency.

3.2.2.2 Modified Form

Clay's performance as an adsorbent material can be improved by making several modifications, including the addition of functional groups, intercalation with surfactant molecules, and its use as a composite material along with other materials (Fatimah, 2018). Modification of clay with APTES (3-aminopropyltrimethoxy silane) reportedly led to no significant change in the surface profile or crystallinity, whereas a higher amount of Pb (II) (from 5–140 mg/L) led to an approximately sevenfold increase in adsorption, as compared to that of raw kaolinite. APTES, which contains N atoms from the ammine functional group, has Lewis base properties, and can potentially bond to a Lewis acid, such as a cation, to allow coordinate chemical bonding (**Figure 5**). The molar ratio of the APTES to the kaolinite weight was varied at 1 mmol/g, 2 mmol/g, 5 mmol/g, and 10 mmol/g, and the corresponding results were encoded as APTES-Kao-01, APTES-Kao-02, APTES-Kao-05, and APTES-Kao-10, respectively. By varying the molar ratio, the adsorption rates yielded the following order: APTES-Kao-10 > APTES-Kao-01 > APTES- Kao-05 > APTES-Kao-02 > kaolinite. The adsorption behavior of Pb ions with kaolinite-modified APTES remained constant at pH values from 6.5 to 10. The formation of Pb species at the hydrolysis pH may compete with adsorption. The adsorption process obeys pseudo-first-order kinetics and fit the Dubinin–Radushkevich isotherm model.

Table 6. Chemical composition of the kaolinite used by Fatimah et al. (2018)

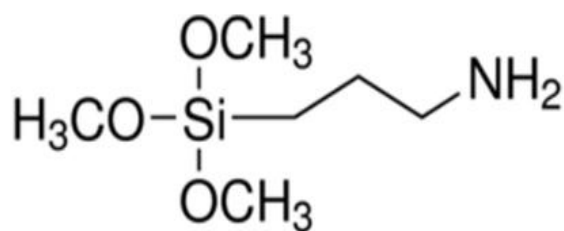| Compound	Mass %
Na_2O	0.13
MgO	0.60
Al_2O_3	25.71
SiO_2	66.56
CaO	0.27
K_2O	6.72

Figure 5. Structure of APTES

Another type of modification technique was used by mixing the biochar of water hyacinth into bentonite (Soetaredjo et al., 2017). This bentonite–biochar nanocomposite is characterized by both microporous and mesoporous structures. Due to its highly porous morphology, the uptake performance of this composite was higher than that of pure bentonite. The maximum adsorption capacities of the bentonite–biochar composite for Cu(II) and Pb(II) were found to be 78.1 mg/g and 44.7 mg/g, respectively. Its adsorption process followed pseudo-first-order kinetics with the parameter k_1 strongly dependent on the temperature. A thermodynamic study was also conducted and the results indicated that the adsorptions of Cu(II) and Pb(II) on both the bentonite and nanocomposite were exothermic and spontaneous.

The use of intercalated bentonite as a lead (II) adsorbent was reported by Nathaniel et al. (2011). The authors intercalated natural bentonite obtained from Pacitan using linear alkylbenzene-sulfonate (LAS) molecules on the interlayer spacing of bentonite to expand its interlamellar spacing. Based on the experimental data, it was obvious that the organo-bentonite had a higher adsorption capacity than natural bentonite (without modification). The sorption process of lead (II) occurred due to the physical interaction, i.e., Van der Waals, between the surface of bentonite and the lead (II) ions. In organo-bentonite, the presence of LAS ions in the bentonite interlayers causes the formation of a negative charge at the adsorbent surface. Accordingly, electrostatic interaction occurs between the negatively charged organo-bentonite and the lead (II) cations, which enhances the sorption capacity. The kinetics data for the adsorption of lead (II) ions onto organo-bentonite was best represented by the pseudo-second-order model, which reveals that the adsorption mechanism also involved a chemical reaction.

Thus, the result findings highlighted that both natural and modified clay minerals have shown the high performance of adsorption capacity for several heavy metal uptakes. In which, the non-modified clay mineral has exhibited the adsorption efficiency as 88% for Pb^{2+} uptake. In addition, the APTES-modified clay minerals have shown the highest adsorption capacity as 140 mg/L for Pb^{2+} removal.

Table 7. Adsorption performances, isotherms, and kinetics of adsorption of heavy-metal ions on Indonesia natural zeolites

Natural Adsorbent	Modification/ treatment	Metal	Adsorption Capacity and Efficiency	Isotherm	Kinetics	References
Clay	Physical mixing with andisol soil	Cd^{2+}	17.9 mg/g	Freundlich	-	(Pranoto et al., 2018)
Clay	-	Pb^{2+} Zn^{2+}	88% for Pb 30% for Zn	Langmuir	-	(Priadi et al., 2014)
Kaolinite	APTES	Pb^{2+}	140 mg/L	Dubinin–Radushkevich	Pseudo-First order	(Fatimah, 2018)
Bentonite	Mixing with water hyacinth biochar	Cu^{2+} Pb^{2+}	78.1 mg/g for Pb 44.7 mg/g for Cu	Langmuir	Pseudo-First order	(Soetaredja et al., 2017)

3.2.3 Fly ash

There are at least four published papers reporting the use of fly–ash waste as a natural adsorbent in Indonesia. The sources of fly ash included waste of coal-fired steam power plant, waste from the textile industry, and the volcanic materials of Mount Kelud (Siswoyo et al., 2016). These different types of fly ash have their own characteristics and properties with respect to the adsorption process.

Fly ash from the Paiton coal-fired steam power plant was used as an adsorbent for mercury (II) and lead (II) ions (Kuncoro et al. 2013). In that study, the fly ash was first heated, then sieved to 250 μm, activated by the addition of CH_3COOH, and heated again at 120 °C for 24 hours. The resulting XRD pattern of fly ash reveals contents of SiO_2 and $CaTiO_3$. In this adsorption study, the authors found that the adsorption capacity of Hg ions was higher than that of Pb. At an initial concentration of 100 ppm, the equilibrium concentration was 50 ppm. Identification by FTIR of the functional groups in the zeolite samples before and after adsorption showed changes in the absorbance values and shifts in several peaks due to the formation of bonds between the functional groups in the adsorbent with Hg and Pb ion molecules (Si-O-Hg and Si-O-Pb).

Furthermore, the study of Pb and Hg adsorption kinetics on fly ash shows that the adsorption characteristics depend on the nature of the fly ash (Kuncoro et al., 2014). Several studies have shown that the adsorption equilibrium point occurs at different times for fly ash originating from different places. The kinetics study of Hg adsorption on fly ash shows the suitability of the rate of pseudo-second-order reactions, wherein the adsorption mechanism involves chemical reactions that occur due to the formation of chemical bonds between the adsorbents and adsorbates. On the other hand,

the adsorption kinetics of Pb ions indicate that the mechanism follows an intra-particle diffusion kinetics model, where surface adsorption occurs in the adsorbent material.

Darmayanti et al. (2017) reported the use of fly–ash waste from coal-fired power plants (FA1) and textile factories (FA2) as copper (II) ion adsorbents. Both fly ashes contained SiO_2, Al_2O_3, MgO, CaO, and Fe_2O_3, with the SiO_2 and Al_2O_3 contents being 52.5% and 48.2%, and 27.8% and 35.4% at FA1 and FA2, respectively. Each adsorbent had a different adsorption performance depending on its chemical content. For each adsorbent, the optimum contact time was 30 min for FA1 and 60 min for FA2, and the optimum dose was 10 g/L, with the FA1 adsorption capacity higher than that of FA2. The presence of more SiO_2 and CaO groups in the FA1 fly ash resulted in a higher FA1 adsorption capacity of 97.39% compared to that of FA2 at 60.07%.

Furthermore, the isotherms identified in the adsorption process resembled a Langmuir-type isotherm. In addition, the adsorption process of Cu (II) on both fly ashes indicated an endothermic reaction, with a negative Gibbs free energy, which indicated that the adsorption process was spontaneous. Analysis of the ΔH (enthalpy change) value of the adsorption indicated that the adsorption process occurs through chemisorption, whereas in the fly ash of FA2, it occurs due to the physical adsorption processes (Darmayanti et al., 2017).
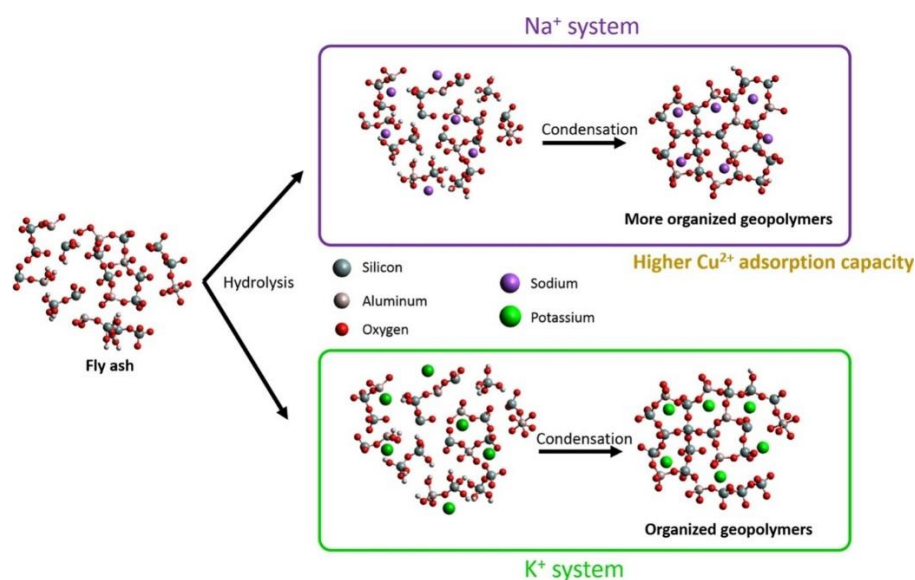

Figure 6. The effect of cations on the structure of geopolymers prepared from fly-ash

(Source: Darmayanti et al., 2019. Reprinted with permission. Copyright Elsevier.)

An interesting adsorption performance result was also reported by Darmayanti et al. (2019) with the use of geopolymers as adsorbent materials. The geopolymers were produced from fly ash and used for Cu^{2+} adsorption. In the synthesis process, fly ash must first be alkali-activated using several systems rich in either an Na^+ or K^+ base. The alkali activation of fly ash could affect the structural alteration and determine its adsorption capacity. The Na^+ activated geopolymer has a more organized

structure than that of the K^+ activated geopolymer, as illustrated in Figure 6. The more organized geopolymer structure exhibited a higher Cu^{2+} adsorption capacity than the original fly ash sample (40 mg/g in comparison to 7 mg/g). The structural change induces the formation of an open-framework structure that provides more accessible sites that can uptake more Cu^{2+} from the solution. This report underlined the importance of designing the materials for specific adsorption purposes.

3.2.4 Bottom ash

The use of bottom ash as an adsorbent has been rarely reported because it contains heavy metals such as manganese (Mn), copper (Cu), zinc (Zn), arsenic (As), lead (Pb), cadmium (Cd), cobalt (Co), chromium (Cr), and nickel (Ni). The presence of these elements can be harmful to the environment as they can leach out into the surrounding soil and groundwater. However, the toxicity characteristic leaching procedure, known as the TCLP test, conducted on bottom ash revealed that the amount of heavy metals leached does not exceed the maximum concentration allowed in their respective country regulations.

Wardani et al. (2018) reported the use of bottom ash as a cadmium (II) ion adsorbent. A comparison of activated bottom ash and that prior to being activated showed a 40.81% increase in adsorption efficiency without activation and 72.47% with activation. However, the process of bottom-ash activation can damage the surface layer of the bottom ash, which is dense, such that its active groups, such as silanol and Al-O-H, can come to the surface. The Cd adsorption process using activated bottom ash showed an optimum contact time of 160 min with an optimum initial concentration of 50 mg/L, the isotherms of which followed the Freundlich model with pseudo-second-order kinetics. In addition, the analysis of the adsorption thermodynamic parameters showed that the reaction process was endothermic, with a decrease in the value of ΔG with rising temperatures such that spontaneous adsorption occurs at higher temperatures. This is because the kinetic energy of the metal ion is high, so more collisions occur between the metal ions and the adsorbate material.

The adsorption capacity of copper (II) with bottom ash using the column method has also shown good results. This adsorption capacity of Cu (II) metal ions on bottom ash was found to be influenced by the flow rate of the column system, whereby the faster was the influent flow rate, the greater was the adsorption capacity. The adsorption capacities of Cu (II) metal ions on bottom ash at flow rates of 1.5 mL/min, 3 mL/min, and 4 mL/min were 79.792 mg/g, 89.507 mg/g, and 96.752 mg/g, respectively. FTIR analysis shows the Cu-O absorption band at 570 cm^{-1}, which indicates that the metal ion Cu (II) was adsorbed onto the oxides in the bottom ash (Setiaka et al., 2011).

Recently, the use of fly ash for the adsorption of copper (II) ion treated with NaOH and KOH was reported by Darmayanti et al. (2018), who found that the adsorption efficiency decreases with increases in the initial concentration of the aqueous solutions for fly ash activated with either NaOH or KOH. This is due to the different surface properties of the fly ash after activation. These data were consistent with the variation in contact time, whereby NaOH-activated zeolite became saturated more slowly than another zeolite with a higher Cu ion uptake. The isotherms of the adsorption process were

found to indicate a monolayer and homogenous-surface Langmuir model. The kinetic study results indicate that the adsorption of copper (II) ions onto both unactivated and activated fly ash correlate to Lagergren's pseudo-second-order reaction.

Thus, the result highlighted that volcanic ash, fly and bottom ash have shown the notable performance of adsorption capacity for heavy metal removal. In which, volcanic ash has shown the adsorption capacity as 82.64 mg/g for Cu^{2+} removal. However, the processed fly ash as geopolymer minerals have shown the highest adsorption capacity in range of 40-54 mg/g for Cu^{2+} removal.

Table 8. Adsorption performances, isotherms, and kinetics of adsorption of heavy-metal ions on Indonesian fly ash

Adsorbent	Modification	Metal	Adsorption Capacity	Isoterm	Kinetics	References
Volcanic ash	-	Cu^{2+}	82.64 mg/g	Langmuir	-	(Siswoyo et al., 2016)
Fly ash	Acetic acid	Hg^{2+} Pb		Langmuir	Intra-particle diffusion	(Kuncoro et al., 2014)
		Cu^{2+}	60.07–97.39 %	Langmuir	Psudo-second order	(Darmayanti et al., 2018)
Fly ash	KOH and NaOH activated	Cu^{2+}	-	Langmuir	Pseudo-second order	(Darmayanti et al., 2017)
Fly ash	Synthesized as Geopolymer	Cu^{2+} Zn^{2+}	47 mg/g for Cu^{2+} 54 mg/g for Zn^{2+}	Langmuir	Pseudo-second order	(Darmayanti et al., 2018)
Fly ash	Synthesized as Geopolymer	Cu^{2+}	40 mg/g	Langmuir	Pseudo-second order	(Darmayanti et al., 2019)
Bottom ash	NaOH	Cd^{2+}	72.47%	Freundlich	-	(Wardani et al, 2018)

4. Conclusion

Local Indonesian natural minerals have been widely investigated for their use as adsorbent materials due to their high performance, availability, and low cost. The adsorption performance of adsorbent materials is highly dependent on the extent of chemical treatment, activation, and modification. Furthermore, the superiority of the properties of natural minerals can be enhanced using certain chemical modifications, as discussed in this review.

This article had reviewed number of reported works conducting the adsorption experiments by using the Indonesian natural minerals under batch technique for heavy metal removal such as cadmium, copper, lead, zinc, chromium (VI), and nickel, and there is comparatively less information available on the adsorption of inorganic pollutants such as mercury, cobalt, manganese, and chromium (III). This review article has also studied the performance of Indonesian natural materials and the adsorption processes in the reported studies were verified by examining the effect of various factors, including pH, contact time, initial concentration, temperature, and dosage. Moreover, the adsorption rate, mechanism, efficiency, their kinetics and thermodynamic parameters of natural materials in the removal of toxic metals from aqueous solution have also been analyzed for examining the performance the adsorbent materials.

Among the natural zeolite materials, the amidoxime-functionalized natural zeolite exhibited the highest adsorption capacity of 72 mg/g to Pb2+ uptakes. In addition, the APTES-modified kaolinites showed the highest adsorption capacity of 140 mg/L within Pb2+ among the clayey materials. However, the natural occurred volcanic ash exhibited highest adsorption capacity of 82.64 mg/g of Cu2+ removal as compared to another both modified and unmodified ashes had been reported. Thus, the high adsorption efficiency rates ranging from 60.07–97.39% and the adsorption capacities up to 140 mg/L indicated the possibility of numerous promising prospects of the material adsorbent in the future.

The previous research of the use of Indonesia natural minerals for heavy metal adsorption had shown significant results. However, further development and method extensions on similar materials are still necessary. Future research opportunities for the use of Indonesia's local natural minerals are still wide open, as the use non-conventional techniques i.e., surfactant modification, functionalizing the adsorbent materials, reducing the particle into the nanosized etc. It needs to be explored to add the value and improve the performance of these natural materials in terms of removal of heavy-metal waste from aqueous solutions.

Author Contribution

Grandprix T. M. Kadja contributed ideas for choosing, text flow, background, methods, data analysis, discussion of results. Moh Mualliful Ilmi background, presentation of results, bibliography.

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