



Polyaniline Modified Natural Zeolite as Adsorbent for Chromium(III) Metal Ion

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Abstract

Zeolite is an inorganic material whose surface has a permanent negative charge in its crystal structure. This material consists of tetrahedral $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$, which are connected by oxygen atoms in such a way as to form an open three-dimensional framework containing canals and cavities, as well as alkali or alkali metals for balancing the negative charge. This structure makes zeolites have the ability to adsorb. The ability of natural zeolite adsorption can improve by modifying the surface by adding polyaniline cationic compounds (PANI), which have an amine group ($:\text{NH}_2$). Moreover, environmental pollution by metals is the biggest problem in daily life, one of which is the metal ion Cr(III), which is a waste from industrial processes. Therefore, it is necessary to have an effort to reduce waste. This study aims to determine the effect of the addition of polyaniline on the adsorption ability of natural zeolites to metal ions Cr(III). The research was carried out in several stages, namely activation of natural zeolite using HF 1%, modification with polymer from aniline monomers, and ammonium peroxodisulphate (APS), and testing the ability of adsorption on Cr(III) metal ions. The study on the ability to adsorb Cr(III) metal ions by PANI-modified zeolites was carried out on variations in the concentration of Cr(III) metal ions and the system pH. The results showed that natural zeolite successfully modified with PANI. The FTIR absorption band at wavenumber $1303-1319\text{ cm}^{-1}$ and 1597 cm^{-1} indicated the presence of NH functional groups. Meanwhile, adsorption capability test data showed that the best adsorbent for adsorption of Cr(III) metal ions was zeolite-PANI 0.01M. The best pH was 4, the initial concentration of Cr(III) metal ions was 1000 ppm, and the percentage of absorption is 48.13%.

1. Introduction

Natural zeolite is an aluminosilicate mineral with a three-dimensional structure, consisting of tetrahedral $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ connected by oxygen atoms. Generally, negatively charged surfaces in natural zeolites balanced by cations of alkali or alkaline earth metal ions. Zeolites have an open three-dimensional skeletal structure, consisting of canals and cavities. Usually, alkali or alkaline earth metals and free moving water molecules [1]. Natural zeolite is one of the most commonly used inorganic materials for surface modification because it has a permanent negative charge in its crystal structure, making it suitable for various types of modifications. The adsorption ability of natural zeolite needs to be improved as in zeolite structure; there are various kinds of

balancing cations such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} , and other metal ions which can cover the pores and cavities of natural zeolites. Activation with acid addition can dissolve the metal oxides and exchange the counter cation to H^+ .

One modification of zeolite carried out by adding cationic compounds to activated zeolites [2]. Polyaniline is a cationic polymer that is widely used to modify natural zeolites because polyaniline has a stable form and has amine groups ($:\text{NH}_2$) and imines (NH^+) in the structure. The amine group ($:\text{NH}_2$) is a potent activator for these compounds due to the resonance and induction effects of the benzene ring. The release of electrons causes the N atom in the group to positively charged, and this is the part that has the potential to interact on negatively

charged surfaces in zeolites [3]. Polyaniline (PANI) modified natural zeolite has been used to remove Cr(VI) in solution [4]. It found that modified zeolite by polyaniline through the polymerization process of anilinium cation. The adsorption capacity of Cr(VI) increased with increasing solution concentration. In the modification of composite nanocellulose (NCC) with polyaniline (PANI) as an adsorbent for Cr (III) and Cr (VI) ions. The results obtained indicated that PANI-NCC had an excellent performance for the adsorption of Cr (VI) and Cr (III) metals 97.89% and 94.12%, respectively [3]. It has been reported by Mir *et al.* [5] that the modification of zeolite nanostructures by PANI has also used in sensing carbon monoxide; heulandite/PANI was used to remove dyes that are acidic efficiently [6]. Recently Jevremović *et al.* [7] reported that BEA/polyaniline zeolites had a higher ability to adsorb nicosulfuron. Also, PANI @ Ni₂O₃-modified zeolite was used as an electrode in the manufacture of hydrogen with photocatalytic water as raw material [8].

Modified natural zeolite with polyaniline (PANI) used as an adsorbent of heavy metal ions as environmental pollution by heavy metals is the biggest problem, with sources of pollution arising from industrial activities. Many toxic metal ions which are very dangerous to animals and humans have been discharged into the environment as industrial waste, causing severe soil and water pollution [9, 10]. One of the dangerous metals found in the environment includes chromium metal. The Chromium(III) is a metal that is quite abundant and becomes a contaminant of various industrial processes [11], such as tanning leather, paint, metallurgy, and hydrocarbon processing. The Cr(III) ion is the most stable oxidation state compared to others, but if there is an oxidizer, then Cr(III) can be oxidized to Cr(VI). Therefore, in this study, the ability of natural zeolites that have modified with polyaniline (PANI) analyzed for the adsorption of Cr(III) metal ion is examined. The zeolite skeletal structure, which has a negative charge on the alumina section, causes electrostatic interactions with positively charged ions (cations), namely polyaniline (PANI). Therefore, it expected that the positively charged Cr(III) metal ion absorbed by the amine group (:NH₂), which turns into a negative charge due to deprotonation in the zeolite-Polyaniline framework. Based on the background, the purpose of this study is to obtain polyaniline modified zeolite (PANI) and determine the ability of adsorption of polyaniline modified zeolite (PANI) to Cr(III) ions based on variations in concentration and pH. A study of the pH effect of the Cr(III) solution is needed as the degree of acidity determines the species in the solution. According to Wu *et al.* [12], in an aqueous solution at pH 2, there are 98% of the chromium species as free Cr³⁺ and 2% as Cr(OH)²⁺. Increasing the pH decreases the Cr³⁺ species and escalates the hydroxide formation. Variation in concentration is needed to determine the ability/capacity of the adsorbents (PANI-modified zeolite) to adsorb.

2. Methodology

2.1. Materials and equipment

Materials: natural zeolite from Bayat, Klaten, Central Java, HF (E. Merck), aniline (E. Merck), HCl (E. Merck), ammonium peroxodisulfate (E. Merck), CrCl₃·6H₂O (E. Merck), distilled water, double distilled water. Equipment: glassware, magnetic stirrer and stirrer bar, shaker (MAXQ 2000), petri dish, filter paper, pH indicator (MERCK), oven (BINDER), OHAUS analytical balance, furnace (VULCAN 3-130), FT-IR spectrometer (Shimadzu), XRF (EQUA), UV-Vis spectrometer (Perkin Elmer).

2.2. Zeolite preparation and activation

A number of natural zeolites were crushed and mashed and then sieved using a 100-mesh sieve, and then washed by distilled water. The residue obtained was heated in an oven at 110°C for 4 hours. A total of 30 grams of zeolite were immersed in 600 mL of 1% HF solution for 10 minutes and stirred at room temperature. Following, zeolite filtered and washed with distilled water until a neutral pH was obtained. The solids resulting from filtration were dried in an oven at 110°C for 4 hours.

2.3. Modification of natural zeolites

2.3.1. Preparation of Aniline-HCl salt

The aniline compound was reacted with 10 mL of concentrated HCl to form aniline-HCl salt which was then sufficiently dissolved in a volumetric flask.

2.3.2. Modification of natural zeolites with polyaniline (PANI)

A total of 0.645 grams of aniline salt and 0.806 grams of ammonium peroxodisulfate (APS) dissolved in 10 mL double distilled water, respectively. Afterward, 5 grams of zeolite was added by 20 mL of the prepared Aniline-HCl solution and stirred for 30 minutes. Then 50 mL of APS (ammonium peroxodisulfate) solution was added to the container under stirring conditions for 2 hours. Then, the mixture was stood for 3 hours, then filtered. Then the residue obtained was washed by a mixture of distilled water and ethanol in a ratio of 1: 4. The washed solids were dried in an oven at 60°C for 5 hours. The aniline-HCl concentration was varied of 0.01 M, and 0.05 M. The polyaniline modified zeolites obtained were then characterized using Fourier-transform infrared spectroscopy (FTIR).

2.4. Chromium ion Adsorption

2.4.1. Variation in concentration

0.1 grams of polyaniline modified zeolite was mixed with 10 mL of CrCl₃·6H₂O solution with a concentration variation of 1000; 1500; 2000; 2500 ppm. The mixtures were shaken for 60 minutes, then filtered. The filtrates were analyzed using a UV-VIS spectrophotometer.

2.4.2. pH variations

A number of 0.1 grams of polyaniline modified zeolite was mixed with 10 mL of CrCl₃·6H₂O with pH variations of pH 1; 2; 3; and 4 at the optimum concentration obtained.

The mixtures were shaken for 60 minutes and then filtered. The filtrates were analyzed using a UV-Vis spectrophotometer.

3. Results and Discussion

1.5. Activation of Natural Zeolites

The natural zeolite used in this study came from Bayat, Klaten, Central Java. The natural zeolite activation can be carried out in two ways, i.e., the physical activation and the chemical activation [13]. The zeolite activation can be physically carried out by grinding zeolites into smaller particles and then sieved with a size of 100 mesh. The scouring and sifting of zeolite are intended to reduce the zeolite size and at the same time, increase the zeolite surface area. Washing and evaporation in the oven at 110°C for 4 hours aimed to clean the zeolite from organic impurities that might cover the zeolite surface, which can interfere with the zeolite modification process. Washing zeolite used 1% HF was intended to open the zeolite pores and remove the oxide impurities (such as CaO, Fe₂O₃, K₂O, and MgO). The metal oxide removal was needed to avoid interference with polyaniline or Cr(III) adsorption. As the natural zeolite is a naturally formed mineral so that the zeolite structure is balancing ions usually vary, including alkaline, alkaline earth, and transition metal group. The interaction between cations of Ca, Mg, and Fe with zeolite structure is reliable, so other these cations needed to be replaced and removed. The existence of these elements can be known from the results of XRF measurements, as shown in Table 1.

During the activation process, it was expected that the structure of the zeolite did not change; hence, the active group possessed by the zeolite became more active to interact with (-NH₂⁺), which was in polyaniline (PANI). The zeolites were dwelled for 10 minutes to maximize the activation process. Next, the zeolites were rinsed by distilled water until a neutral pH obtained. The zeolites obtained were referred to as activated zeolites. After that, the activated zeolites were heated in an oven at 110°C for 4 hours in order to remove water and solvents trapped in zeolite pores [14].

1.6. Modification of activated zeolite with polyaniline (PANI)

The nitrogen atom in the imine group contained in polyaniline can form -NH₂⁺ so that it has the potential to interact with the zeolite surface, which has a negative charge. This modification was carried out with variations in concentrations of 0.01 and 0.05 M. It was expected that cation exchange occurred between the hydronium ion and the ammonium group. The change in color indicates a zeolite-PANI interaction. At the addition of 0.01 M aniline-HCl, the grayish-white color of active zeolite turned became a dark gray, while at the concentration of 0.05 M, the color became darker, as shown in Figure 1. These color changes indicate that the formation of polyaniline polymers has been successful.

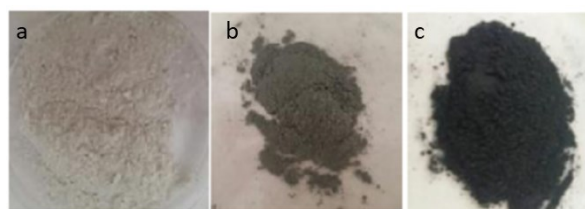
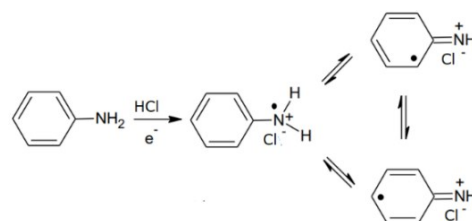


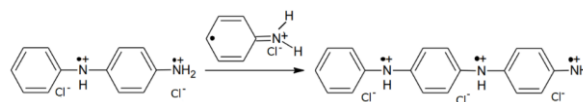
Figure 1. Color changes in (A) natural zeolite (B) 0.01-PANI zeolite (C) 0.05M zeolite-PANI

Polyaniline modified zeolite (zeolite-PANI) was obtained by adding aniline monomers (C₆H₅NH₂) and HCl to the zeolite structure, then adding ammonium peroxodisulfate (APS) NH₄S₂O₈. The polyaniline formation was the result of the polymerization of aniline with an HCl as an oxidizer. The polymerization began with the initiation step in the acid atmosphere, and this stage required high energy. APS was used as an initiator agent which has a higher oxidation potential than aniline [15]; hence, protons in acids could bind with amine groups to form Ani-HCl. According to Wallace *et al.* [16], the formation of polyaniline polymers from aniline is as follows:

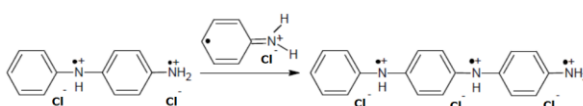
1. Initiation step



2. Coupling step



3. Propagation step



4. Termination step

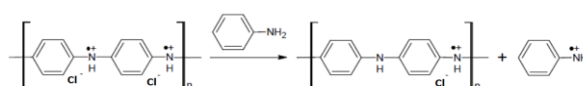


Figure 2 shows an illustration of the formation of Zeolite-PANI in which N atoms bound to the imine group of polyaniline can form -NH₂⁺. It predicted that interactions with the negative charge could occur on the surface of the zeolite.

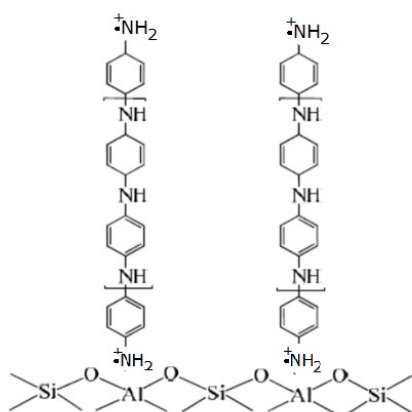


Figure 2. Illustration of zeolite–PANI formation

1.7. Effect of addition of PANI on the composition of zeolite components

In the activation process, the addition of 1% HF aimed to dissolve or remove other metals found inside the zeolite framework. The existence of these metals can be determined through elemental analysis using X-ray Fluorescence (XRF). The XRF measurement data listed in Table 1.

Table 1 shows that the activation process causes a decrease in the amount of metal, even though the metal does not completely disappear. Activated zeolite still contains calcium and iron ions. Strong interactions between zeolites and calcium and iron make removal of the counterweight cation not easy.

Table 1. Component on natural zeolites and zeolites–PANI

| Components | Content (%) | | |
|--------------------------------|-----------------|--------------------|--------------------|
| | Natural zeolite | Zeolite–PANI 0.01M | Zeolite–PANI 0.05M |
| SiO ₂ | 66.58 | 72.90 | 56.04 |
| Al ₂ O ₃ | 10.75 | 9.90 | 7.75 |
| CaO | 8.10 | 5.90 | 5.12 |
| Fe ₂ O ₃ | 5.37 | 4.35 | 3.99 |
| K ₂ O | 5.63 | 2.56 | 1.79 |
| Cl | 1.02 | 1.07 | 1.61 |
| SO ₃ | 1.07 | 1.01 | 3.90 |
| TiO ₂ | 1.00 | 0.84 | 0.89 |

Table 1 also indicates that the Si/Al ratios increase due to the modification of zeolite with polyaniline. The Si/Al ratio increases from 10.94 on natural zeolites to 13.546 for zeolite–PANI 0.01 M and to 12.77 on zeolite–PANI 0.05 M, respectively. Increasing the Si / Al ratio is expected to reduce the negative charge on the zeolite surface.

1.8. FTIR analysis results

Infrared spectra analysis (FTIR) is an important method to characterize the structure of the framework. The spectra of zeolite before and after modification by PANI were shown in Figure 3.

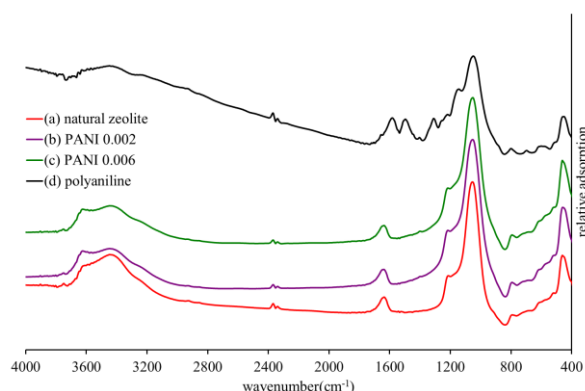


Figure 3. FTIR spectra of natural zeolite and zeolite–PANI

Figure 3 displays the FTIR spectra of zeolite. The zeolite framework structure was shown in the wavenumber region of 300–1300 cm⁻¹ in which indicate the existence of tetrahedral [SiO₄]⁻⁴ and [AlO₄]⁻⁵ bonds. The wavenumber 420–500 cm⁻¹ is the vibration of Si–O/Al–O (T–O) on the internal, while the wave number 700–780 cm⁻¹ is the vibration of the Si–O/Al–O (T–O) on the external. The symmetrical range is shown at wavenumbers 650–850 cm⁻¹, and the asymmetric range is shown at wavenumbers 900–1250 cm⁻¹ [17].

The comparison of the FTIR spectrum of polyaniline and PANI–modified zeolites explain the protonation of PANI. The wavelength of about 1335–1250 cm⁻¹ demonstrates the presence of stretching C–N bond is considered to be a measure of the degree of electron delocalization in the PANI chain. It is thus a characteristic peak associated with the conductivity of the PANI because, in its structure, it has a conjugated yang bond, which causes electrons to move along the structure. The formation of a PANI polymer occurs through the interaction of –NH₂ groups and carbonium ions in phenyl to form a C–N bond. The absorption intensity at C–N increases with increasing PANI concentration in zeolites [3]. In addition, FTIR spectra show that Polyaniline (PANI) can interact with activated zeolites through cation exchange. This is evidenced by the emergence of the peak of Polyaniline with a wavelength of around 116–1176.28 cm⁻¹, which is a C–H bending vibration and at a wavelength of about 1400–1500 cm⁻¹ which is a C=C benzenoid vibration and 1500–1600 cm⁻¹ which is the vibration of C=C quinoid [18].

Figure 3 also shows that variations in concentration affect the position, shape, and peak absorption of zeolite–PANI. The higher the concentration of polyaniline added to zeolite, the more it shows the spectral shape, which is close to the polyaniline spectra. The interaction between zeolite and polyaniline is likely a physical interaction. This is characterized by the non-generation of new groups that characterize the bond between zeolite and polyaniline, but only show the combination of functional groups of zeolite and polyaniline.

To find out the change in intensity, it is necessary to have a quantitative analysis. The analysis was conducted using a Fityx application where FTIR spectra were derived

into the constituent peaks with a Gaussian approach. Previously, FTIR spectra were normalized, and the derivation curve was compared by equalizing the Half-width at half maximum (HWHM) of each derivation peak. Then, the derivative peaks were compared with the peak of Si-O-Si. The peak deconvolution results obtained were available to obtain information about almost imperceptible differences (vibrations in overlapping regions) in the modification process by measuring the absorption intensity that is related to the type of chemical group to be measured. The calculation results are in Table 2.

Table 2. The results of calculating the C-H/Si-O ratio

| Sample | The absorption intensity of the function group | | The ratio of C-H/Si-O |
|-------------------|--|------------------------------|-----------------------|
| | Si-O (1050 cm ⁻¹) | C-H (1162 cm ⁻¹) | |
| Natural zeolite | 22564 | 267.66 | 1.1862 |
| Zeolite-PANI 0.01 | 23536.9 | 896.84 | 3.8103 |
| Zeolite-PANI 0.05 | 24059.1 | 1404.29 | 5.8369 |

The deconvolution results show that the addition of polyaniline increases the CH / Si-O-Si ratio, which is in accordance with the prediction that the addition of polyaniline increases the carbon content in zeolite-PANI.

1.9. Application of Zeolite-PANI as chromium(III) metal ion adsorbent

Polyaniline (PANI) modified natural zeolite adsorption capability on Cr(III) metal ions was carried out at initial concentration variations of 1000, 1500, 2000, and 2500 ppm as well as variations in system pH 1,2,3 and 4. The concentration of Cr(III) ions after adsorption was analyzed using a UV-Vis spectrophotometer at a maximum wavelength of 420 nm. The graph of the relationship of Cr(III) metal ion concentration with adsorbed efficiency in three samples of zeolite-PANI 0.01 M, zeolite-PANI 0.05 M and natural zeolite can be seen in Figure 4, while the graph of the relationship between system pH and adsorption efficiency of metal ions adsorbed contained in Figure 5.

In Figure 4, it observed that the adsorption capacity of Cr(III) metal ions by activated zeolites and zeolites-PANI decreases with increasing concentration of a metal solution. These conditions indicate that the active sites of natural zeolite and zeolite-PANI adsorbents at high concentrations have saturated by these Cr(III) metal ions. Hence the adsorption capacity tends to decrease at high concentrations. The adsorption process through electrostatic interaction between the positive charge contained in Cr(III) and the negative charge of polyaniline deprotonated to (-NH₂⁺), so that interaction can occur because zeolites and polyanilines have formed a bilayer on the outer surface of zeolite above the surface [19].

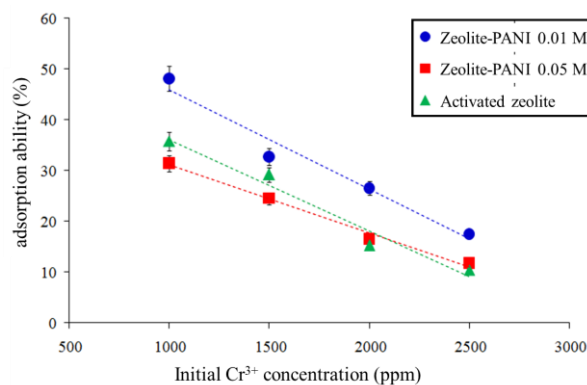


Figure 4. Graph of the relationship of Cr(III) metal ion concentration with adsorption efficiency in zeolite-PANI 0.01 M, zeolite-PANI 0.05 M, and natural zeolites

The attraction between these charges causes lower concentrations of Cr(III) metal ions to make the ability to adsorb between molecules more easily because they only require less energy. In addition, the efficiency of adsorbed Cr(III) is not too high <50%, due to the charge that exists along the PANI polyelectrolyte chain which is bound to the active center of the zeolite causing a repulsive force between the charge contained in the PANI which is fully charged so that the Cr(III) metal ion, it is difficult to enter the zeolite-PANI group.

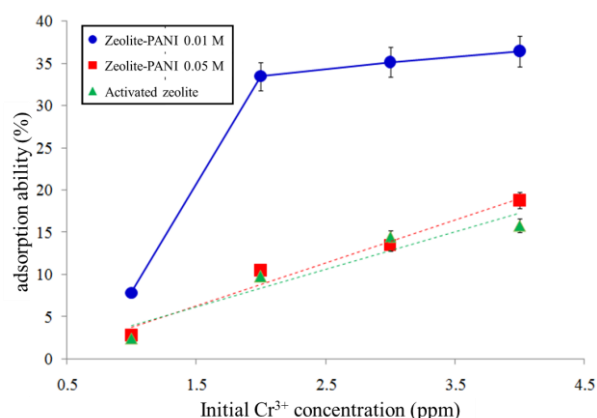


Figure 5. Graph of the relationship between pH and % adsorption efficiency Cr(III) by zeolite-PANI 0.01 M, zeolite-PANI 0.05 M and natural zeolite

The pH conditioning was carried out on the Cr(III) solution before it has interacted with zeolite. The choice of pH 1-4 in the adsorption process was due to chromium being in the form of free Cr(III) or Cr³⁺ at pH 1-2, at the higher pH, the concentration of Cr³⁺ begins to decrease, and Cr(OH)²⁺ starts to appear. If the pH was higher, it was possible that adsorption could interfere with the deposition of Cr(OH)₃. Sulastrri *et al.* [20] showed that in a solution with a low pH, the Cr(III) ion dissolved, and experienced turbidity in a solution with a pH of 5.

To get optimum pH conditions, the concentration of Cr(III) metal ion 1000 ppm was used because this concentration was absorbed most by activated zeolite and zeolite-PANI. Based on Figure 5, the highest adsorption efficiency of Cr(III) metal ions by activated zeolite and zeolite-PANI was at pH 4. At pH 1-4, the adsorption

efficiency increases as at high pH, the zeolite-PANI deprotonated to form a negative charge surface (:NH_2^-) and able to absorb Cr(III) cationic through electrostatic interactions. The increase in pH also causes the amount of -NH_2^- in zeolite-PANI to form more; hence, the bonds that occurred between Cr(III) ions and the active group of nitrogen atoms also increased. The adsorption result at pH 1 shows that adsorbed efficiency is much smaller compared to other pH levels. This is because, in conditions that are too acidic, pH may damage the structure of zeolites. Damage to the structure can occur because the Al metal in the zeolite is separated from the structure in the framework [21], resulting in a negative charge on the zeolite decreases, which makes the absorption power to absorb Cr(III) metal ions decreases [22]. Besides, there is the possibility of competition between H^+ and Cr(III) metal ions to be adsorbed by zeolites.

At an alkaline pH caused the solution of Cr(III) to settle. This is because the Cr(III) ion has a K_{sp} value of around 3.752×10^{-3} , so based on the calculation of the Cr(III) ion, it will settle to a $\text{pH} > 5.29$ [23]. At the time of basic conditioning, ammonia solution is added to the pH showing > 5.29 , and deposition occurs like gelatin, which is gray-green to blue-gray, namely chromium(III) hydroxide [24].

4. Conclusions

It is concluded that the natural zeolite had been successfully modified by PANI, which was characterized by the presence of polyaniline groups at wavenumbers $1303\text{--}1319\text{ cm}^{-1}$ and 1597 cm^{-1} in the FTIR spectra. The ability of adsorbent adsorbents in the form of the best adsorption efficiency of Cr(III) metal ions was 0.01 M zeolite-PANI at pH of 4 and at an initial concentration of 1000 ppm which was in the value of 48.13%.

References

- [1] Balwinder Kaur and Rajendra Srivastava, Simultaneous determination of epinephrine, paracetamol, and folic acid using transition metal ion-exchanged polyaniline-zeolite organic-inorganic hybrid materials, *Sensors and Actuators B: Chemical*, 211, (2015) 476–488 <https://doi.org/10.1016/j.snb.2015.01.081>
- [2] Anis Komariah, Sriatun Sriatun and Pardoyo Pardoyo, Adsorpsi Alkil Benzene Sulfonat Menggunakan Zeolit Termodifikasi Cetyltrimethylammonium, *Jurnal Kimia Sains dan Aplikasi*, 20, 1, (2017) 13–18 <https://doi.org/10.14710/jksa.20.1.13-18>
- [3] Priyanka Jain, Shilpa Varshney and Shalini Srivastava, Site-specific functionalization for chemical speciation of Cr(III) and Cr(VI) using polyaniline impregnated nanocellulose composite: equilibrium, kinetic, and thermodynamic modeling, *Applied Water Science*, 7, 4, (2017) 1827–1839 <https://doi.org/10.1007/s13201-015-0356-1>
- [4] Abdulsalam A. Shyaa, Omar A. Hasan and Ahmed M. Abbas, Synthesis and characterization of polyaniline/zeolite nanocomposite for the removal of chromium(VI) from aqueous solution, *Journal of Saudi Chemical Society*, 19, 1, (2015) 101–107 <https://doi.org/10.1016/j.jscs.2012.01.001>
- [5] Muzzaffar Ahmad Mir, Muzzaffar Ahmad Bhat, Sheikh Abdul Majid, Shabir H. Lone, Manzoor Ahmad Malla, Kautilya Rao Tiwari, Ashiq Hussain Pandit, Radha Tomar and Rayees Ahmad Bhat, Studies on the synthesis and characterization of polyaniline-zeolite nanostructures and their role in carbon monoxide sensing, *Journal of Environmental Chemical Engineering*, 6, 1, (2018) 1137–1146 <https://doi.org/10.1016/j.jece.2018.01.027>
- [6] Mostafa R. Abukhadra, Mohamed Rabia, Mohamed Shaban and Francis Verpoort, Heulandite/polyaniline hybrid composite for efficient removal of acidic dye from water; kinetic, equilibrium studies and statistical optimization, *Advanced Powder Technology*, 29, 10, (2018) 2501–2511 <https://doi.org/10.1016/j.apt.2018.06.030>
- [7] Anka Jevremović, Patrycja Bober, Matej Mičušík, Jaroslav Kuliček, Udit Acharya, Jiří Pflieger, Maja Milojević-Rakić, Danina Krajišnik, Miroslava Trchová, Jaroslav Stejskal and Gordana Čirić-Marjanović, Synthesis and characterization of polyaniline/BEA zeolite composites and their application in nicosulfuron adsorption, *Microporous and Mesoporous Materials*, 287, (2019) 234–245 <https://doi.org/10.1016/j.micromeso.2019.06.006>
- [8] Mohamed Adel Sayed, Mostafa R. Abukhadra, Mohamed Abdel Salam, Sobhy M. Yakout, Ahmed A. Abdeltawab and Ibrahim M. Aziz, Photocatalytic hydrogen generation from raw water using zeolite/polyaniline@Ni₂O₃ nanocomposite as a novel photo-electrode, *Energy*, 187, (2019) 115943 <https://doi.org/10.1016/j.energy.2019.115943>
- [9] Afshin Maleki, Bagher Hayati, Maryam Naghizadeh and Sang W. Joo, Adsorption of hexavalent chromium by metal organic frameworks from aqueous solution, *Journal of Industrial and Engineering Chemistry*, 28, (2015) 211–216 <https://doi.org/10.1016/j.jiec.2015.02.016>
- [10] Rania E. Morsi, E. A. Khamis and A. M. Al-Sabagh, Polyaniline nanotubes: Facile synthesis, electrochemical, quantum chemical characteristics and corrosion inhibition efficiency, *Journal of the Taiwan Institute of Chemical Engineers*, 60, (2016) 573–581 <https://doi.org/10.1016/j.jtice.2015.10.028>
- [11] Nomcebo H. Mthombeni, Maurice S. Onyango and Ochieng Aoyi, Adsorption of hexavalent chromium onto magnetic natural zeolite-polymer composite, *Journal of the Taiwan Institute of Chemical Engineers*, 50, (2015) 242–251 <https://doi.org/10.1016/j.jtice.2014.12.037>
- [12] Deyi Wu, Yanming Sui, Shengbing He, Xinze Wang, Chunjie Li and Hainan Kong, Removal of trivalent chromium from aqueous solution by zeolite synthesized from coal fly ash, *Journal of Hazardous Materials*, 155, 3, (2008) 415–423 <https://doi.org/10.1016/j.jhazmat.2007.11.082>
- [13] Dewi Yuanita Lestari, Kajian modifikasi dan karakterisasi zeolit alam dari berbagai negara, Prosiding Seminar Nasional Kimia dan Pendidikan Kimia 2010, Yogyakarta, (2010).
- [14] Sofian Ansori, Sriatun Sriatun and Pardoyo Pardoyo, Modifikasi Zeolit Alam Menggunakan TiO₂ sebagai

- Fotokatalis Zat Pewarna Indigo Carmine, *Jurnal Kimia Sains dan Aplikasi*, 19, 2, (2016) 68–71
<https://doi.org/10.14710/jksa.19.2.68-71>
- [15] Iman Rahayu, Annisa Wijayati and Sahrul Hidayat, Sintesis dan Karakterisasi Polianilina Doping Asam Klorida dengan Metode Interfasial, *Jurnal Kimia VALENSI: Jurnal Penelitian dan Pengembangan Ilmu Kimia*, 2, 1, (2015) 74–79
<https://doi.org/10.15408/jkv.voio.3143>
- [16] Gordon G. Wallace, Peter R. Teasdale, Geoffrey M. Spinks and Leon A.P. Kane-Maguire, *Conductive Electroactive Polymers: Intelligent Materials Systems*, Second Edition, CRC Press, 2002.
- [17] Halimatun Hamdan, *Introduction To Zeolites: Synthesis, Characterization, and Modification*, Universiti Teknologi Malaysia, Kuala Lumpur, 1992.
- [18] A. Olad, M. Khatamian and B. Naseri, Removal of toxic hexavalent chromium by polyaniline modified clinoptilolite nanoparticles, *Journal of the Iranian Chemical Society*, 8, 1, (2011) S141–S151
<https://doi.org/10.1007/BF03254291>
- [19] Silvio R. Taffarel and Jorge Rubio, Removal of Mn²⁺ from aqueous solution by manganese oxide coated zeolite, *Minerals Engineering*, 23, 14, (2010) 1131–1138
<https://doi.org/10.1016/j.mineng.2010.07.007>
- [20] Siti Sulastris, Indriana Kartini Nuryono and Eko Sri Kunarti, Kinetika dan Keseimbangan Adsorpsi Ion Kromium (III) dalam Larutan pada Senyawa Silika dan Modifikasi Silika Hasil Sintesis dari Abu Sekam Padi, *Jurnal Penelitian Saintek*, 19, 2, (2014) 33–44
- [21] Sriatun Sriatun, Dimas Buntarto and Adi Darmawan, Pengaruh Penambahan Surfaktan Hexadecyltrimethyl-Ammonium (HDTMA) pada Zeolit Alam Terdealuminasi terhadap Kemampuan Mengadsorpsi Fenol, *Jurnal Kimia Sains dan Aplikasi*, 11, 1, (2008) 11–14
<https://doi.org/10.14710/jksa.11.1.11-14>
- [22] Tom Chih-Hung Wang, Polyelectrolyte multilayers as nanostructured templates for inorganic synthesis, Massachusetts Institute of Technology,
- [23] Tan Chen, Zeyu Zhou, Sai Xu, Hongtao Wang and Wenjing Lu, Adsorption behavior comparison of trivalent and hexavalent chromium on biochar derived from municipal sludge, *Bioresource Technology*, 190, (2015) 388–394
<https://doi.org/10.1016/j.biortech.2015.04.115>
- [24] G. Svehla, *Vogel's Qualitative Inorganic Analysis*, Pearson Education, 2008.