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Determination Point of Zero Charge (PZC) of nZVI-MXene Adsorbent for Reduction of Ciprofloxacin Contaminants in Wastewater

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Abstract
Ciprofloxacin is an antibiotic commonly used for bacterial infections. It is found in significant concentrations in hospital outlet wastewater and the pharmaceutical industry. Nano zero-valent iron (nZVI) has strong reducing power, and MXene is known for its anti-corrosion. Achieving effective results in this adsorption process is influenced by several factors, such as pH. The point of zero charge is the pH at which the material's surface is electrically neutral.The pH pzc was measured by adding the material to a 0.01 M $NaNO_3$ solution with an initial pH of 2–12, shaking for 2 hours, leaving for 2 days, and measuring the final pH of each solution. The pH pzc on nZVI material is 4.25. The pHpzc of the MXene material is 2.8. The pHpzc on the nZVI-MXene material is 3.45. The pHpzc value on the nZVI-MXene material is lower than nZVI and higher than MXene. The presence of acid groups from MXene, which dominate the surface of the material, can cause the pHpzc value to be closer to the pHpzc value of MXene than nZVI but still higher than MXene due to the influence of the base group from nZVI. In addition to electrostatic interactions, other mechanisms exist during high pH reactions, such as interactions of active functional groups on the material's surface with adsorbates through chemical bonds.
Keywords: *adsorption, antibiotic, hospital outlet wastewater, pharmaceutical industry,* pH_{pzc}

Abstrak
Ciprofloxacin merupakan antibiotik yang umum digunakan untuk mengatasi infeksi akibat bakteri. Zat ini ditemukan dalam konsentrasi yang signifikan di air limbah rumah sakit dan di industri farmasi. Besi nano-valen nol (nZVI) memiliki daya reduksi yang kuat dan MXene dikenal karena sifat anti korosinya. Pencapaian hasil yang efektif dalam proses adsorpsi dipengaruhi oleh beberapa faktor seperti pH. Titik muatan nol adalah pH di mana permukaan material bersifat netral secara elektrik. Pengukuran pH pzc dilakukan dengan menambahkan material dalam larutan $NaNO_3$ 0,01 M dengan pH awal 2–12, dikocok selama 2 jam dan dibiarkan selama 2 hari, lalu diukur pH akhir setiap larutan. Nilai pH pzc pada material nZVI adalah 4,25, pada material MXene adalah 2,8, dan pada material nZVI-MXene adalah 3,45. Nilai pH_{pzc} pada material nZVI-MXene lebih rendah daripada nZVI dan lebih tinggi daripada MXene. Adanya gugus asam dari MXene yang mendominasi permukaan material, dapat menyebabkan nilai pH_{pzc} lebih mendekati nilai pH_{pzc} MXene daripada nZVI tetapi masih lebih tinggi daripada MXene karena adanya pengaruh gugus basa dari nZVI. Selain interaksi elektrostatik, terdapat mekanisme lain selama reaksi pH tinggi, seperti interaksi gugus fungsi aktif pada permukaan material dengan adsorbat melalui ikatan kimia.
Kata Kunci: *adsorpsi, antibiotik, limbah rumah sakit, industri farmasi,* pH_{pzc}

1. Introduction

Antibiotics play an important role in the pharmaceutical world. This is evidenced by the concentration of antibiotic substances detected entering the environment reaching 30-90% and the content of substances detected in pharmaceutical wastewater reaching 100-500 mg/L [1]. Ciprofloxacin (CPFX) is an antibiotic commonly used for infections caused by bacteria in both human and animal medicine [2]. CPFX found in hospital outlet wastewater and from the pharmaceutical industry has a significant concentration [3]. In previous studies, the detected CPFX content in pharmaceutical wastewater ranged from 31-50 mg/L [4]. Meanwhile, in a study of surface water flow samples, the CPFX concentration ranged from 2.5-6.5 mg/L [5]. The CPFX content found in studies of surface water concentrations in several countries such as Argentina, China, and Vietnam ranges from 0.25-7.7 μg/L, while in India, it can reach

5,528 µg/L [6]. Research on CPFX content in Wastewater Treatment Plants (WWTP) in several countries, such as the United States, South Korea, and Pakistan, ranges from 1.3-341 µg/L. In comparison, in Portugal, hospital waste was detected at 38.6 µg/L [6]. Therefore, it is necessary to treat wastewater containing CPFX so that it is not harmful to living things and the surrounding environment.

There are several ways to reduce the concentration of CPFX in effluent water from Wastewater Treatment Plants (WWTP), one of which is by modifying nanoparticles to reduce the concentration of CPFX in water bodies. The advantage of using these nanoparticles is that the material properties (surface area, reactivity, adsorption capacity) are more consistent because the particle size is homogeneous [1]. This study will use nano Zero Valent Iron (nZVI) and MXene (Ti3C2Tx). The advantages of nZVI are that the particles are small, have strong reducing power, and have good reactivity and magnetic separation [7]. Several previous studies have shown that this nZVI nanocomposite can effectively reduce antibiotic and dye content in a water body. MXene is a material that has two new dimensional layers and is known for its anti-corrosion and anti-wear properties, so it is currently developing rapidly [8]. MXene has the chemical formula Mn+1XnTx (n = 1 ~ 4), where M represents a transition metal element, X is a carbon or nitrogen, and Tx is a surface functional group like -OH, -F, -O [9]. This transition metal core layer is conductive to facilitate high-speed electron transfer. Based on previous studies, achieving effective results in this adsorption process is influenced by several factors, including the adsorbent's characteristics and pore size and the adsorbate's solubility. In addition, there are also external factors from the environment, such as pH, temperature, and contact time of the adsorbent and adsorbate. The pH susceptible to ciprofloxacin if in control conditions without treatment is 3.3-3.9 [10].

According to previous research, the zero charge point (pH_{pzc}) will be analyzed to determine the adsorption efficiency. At a pH less than pHpzc of the nanoparticles, the surface of the nanoparticles will have a positive charge due to the protonation of their active groups. In contrast, CPFX, which is amphoteric, will have a negative charge ($CPFX^-$) because its carboxylate group is deprotonated. Conversely, if the pH value is higher than pHpzc, the surface of the nanoparticles will experience deprotonation and become negatively charged. In contrast, CPFX will be positively charged ($CPFX^+$) due to the protonation of the amino group [11]. This study will measure the pH_{pzc} on nZVI and MXene and determine its effect on ciprofloxacin.

2. Material and Methods

2.1 Materials

Materials used in this study include nZVI nanoparticles as adsorbents. MXene as adsorption material. nZVI-MXene nanocomposite with a ratio of nZVI : MXene of 2:1 as an adsorbent with higher adsorption capacity. According to previous studies, the comparison of nZVI and Mxene composites was reinforced by findings from other studies. An analysis of the physical properties of N-Mxene-1, N-Mxene-2, and N-Mxene, corresponding to ratios of 1:1, 1:2, and 2:1 respectively, indicated that the 2:1 ratio exhibited superior properties and surface area [12].

Moreover, the tested ratios of nZVI-Mxene nanocomposites were 1:2, 1:1, 2:1, and 3:1. This study found that the percentage of metronidazole removal was highest at a 2:1 ratio, achieving a notable removal rate of 90.89% after 90 minutes. In contrast, increasing the nZVI ratio beyond 2:1 resulted in a decrease in removal efficiency. This suggests that surpassing the 2:1 ratio caused the aggregation of iron particles, which hindered electron transfer [13].

2.2 Chemicals

During the experiment, HNO_3 0,1 M and NaOH 0,1 M lowered and increased pH and were used to condition the base and acid in the ciprofloxacin solution. $NaNO_3$ 0,01 M is used as an inert electrolyte solution to maintain ion stability.

2.3 Determination of pH pZC

The process of testing and determining pH Point Zero Charge (pH_{pzc}) is a condition when the surface of the adsorbent is neutrally charged. PZC is obtained from the results of the intersection point between the pH curve at the initial and final conditions of the treatment. The method of determining pH_{pzc} for nZVI nanoparticles, MXene, and nZVI-Mxene nanocomposites is to insert a 0,01 M $NaNO_3$ solution as much as 50 mL into several 100 mL Erlenmeyer flakes. The initial pH is adjusted within the range of 2-12 using 0,1 M HNO_3 or 0,1 M NaOH, measured with a digital pH meter (Kedida pH Conductivity Meter CT6321). After that, each Erlenmeyer is added with 0.2 grams of nZVI nanoparticles, MXene, and nZVI-Mxene nanocomposites. The mixture is agitated using a mechanical shaker (IKA KS 260) at 200 rpm for 2 hours

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to ensure proper interaction. After shaking, the solution is left undisturbed for 2 days at room temperature (± 25°C). The final pH is then measured using the same digital pH meter, and the pH pzc is determined from the intersection of the initial and final pH curves.

3. Results and Discussion

The point of zero charge (pH_{pzc}) is the pH at which the material's surface is electrically neutral. At a pH less than pH pzc ($pH < pH_{pzc}$), the material's surface will be positively charged. The material's surface will be negatively charged if the pH is less than pH_{pzc} ($pH > pH_{pzc}$). The results of the calculation and analysis of pH_{pzc} on each material on each material are shown in Table 1. where the initial pH or initial pH is symbolized by pH_i. PH_a symbolizes the final pH, and ΔpH symbolizes the result of subtracting the initial and final pH.

Table 1. Results of testing and analysis of pH pzc

pH_i	nZVI		MXene		nZVI-MXene	
	pH_a	ΔpH	pH_a	ΔpH	pH_a	ΔpH
2	3,42	-1,42	3,79	-1,79	2,21	-0,21
3	4,70	-1,70	2,77	0,23	3,69	-0,69
4	4,21	-0,21	3,64	0,36	3,04	0,96
5	4,61	0,39	3,49	1,51	3,15	1,85
6	4,58	1,42	3,36	2,64	3,87	2,13
7	4,86	2,14	3,42	3,58	3,47	3,53
8	5,80	2,21	3,49	4,51	4,70	3,30
9	4,78	4,22	4,13	4,87	3,38	5,62
10	6,59	3,41	5,57	4,43	5,53	4,47
11	8,47	2,53	7,52	3,48	7,73	3,27

Based on **Table 1** pH $_{pzc}$ can be determined by graphing between pHi as the x-axis and ΔpH as the y-axis, where pH pzc can be obtained when the point on the ΔpH graph is zero (ΔpH = 0). In this condition, the material's surface is electrically neutral.

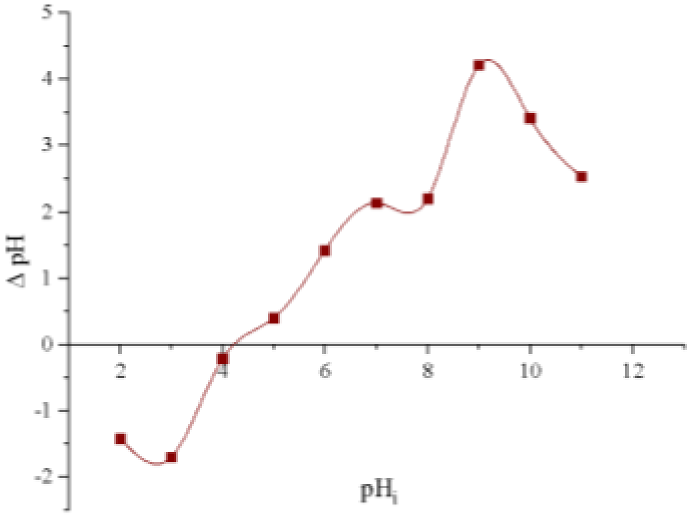

Figure 1. pH_{pzc} nZVI determination graph

Based on **Figure 1** pH_{pzc} on nZVI material is 4.25. According to previous research, when the pH is higher, H+ ions will be in solution rather than on the material's surface so that the material's surface will have a negative ion charge [14]. In this study, at a higher pH, CPFX will have a positive ion charge, which causes electrostatic attraction between the surface of nZVI and CPFX+, which supports increased adsorption efficiency.

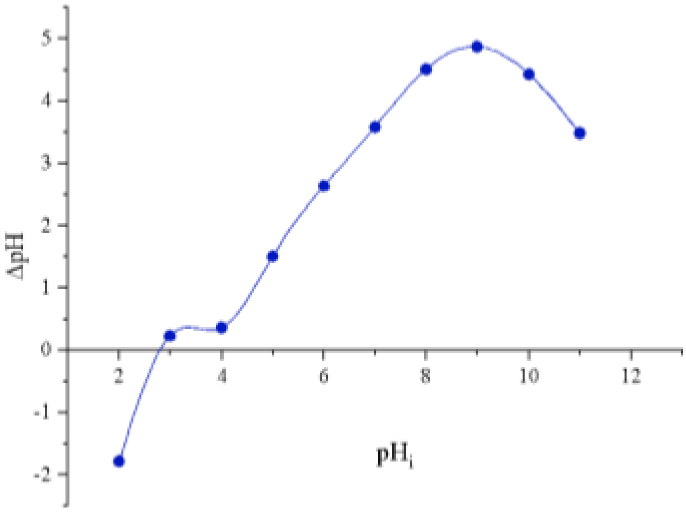

Figure 2. pH_{pzc} MXene determination graph

Meanwhile, **Figure 2** shows that the pHpzc of the MXene material is 2.8. The pHpzc value of the MXene material is lower than that of nZVI. This result can be due to the use of HF etching agents during the MXene synthesis process to strengthen the strong acid functional groups, in contrast to nZVI, which is usually produced from Fe reduction and has a more basic surface due to its oxide and hydroxide content [15]. According to previous research, when the pH is higher, H+ ions will be in solution rather than on the material's surface so that the material's surface will have a negative ion charge [14]. In this study, the MXene surface has a very negative ion charge at a higher pH due to the low pHpzc value. CPFX has a positive ion charge (CPFX+) at that pH, so a strong electrostatic attraction occurs between the MXene and CPFX surfaces [14].

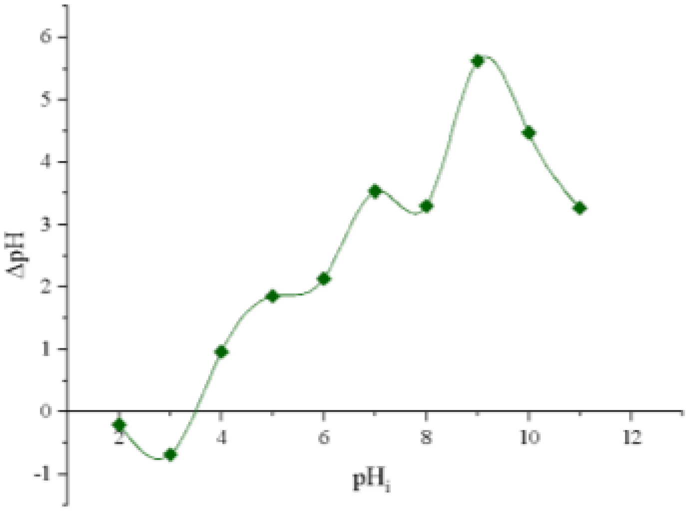

Figure 3. pH_{pzc} nZVI-MXene determination graph

Meanwhile, **Figure 3** shows that the pHpzc on the nZVI-MXene material is 3.45. The pHpzc value on the nZVI-MXene material is lower than nZVI and higher than MXene. This result is due to the presence of acid groups from MXene, which dominate the surface of the material, which can cause the pHpzc value to be closer to the pHpzc value of MXene than nZVI but still higher than MXene due to the influence of the base group from nZVI. In this study, the surface of nZVI-MXene has a very negative ion charge at a higher pH due to the low pHpzc value. CPFX has a positive ion charge (CPFX+) at that pH. Hence, a strong electrostatic attraction occurs between the surface of nZVI-MXene and CPFX, which is stated in previous research on the electrostatic properties of materials when they are zero-charged [14].

Previous studies tested the effectiveness of adsorbent removal of CPFX content with pH conditioning of 5, 7, and 9. This study obtained the pH with the highest removal efficiency at pH 9. In addition to electrostatic interactions, other mechanisms exist during high pH reactions, such as interactions of active functional groups on the material's surface with adsorbates through chemical bonds. There are other factors that cause the highest removal efficiency to occur at pH 9, namely the ionic form of CPFX at each different pH. At pH 5 and 7, CPFX has a weak cation charge. In contrast, at pH 9, CPFX is more susceptible to attack by active species than the cationic form due to the higher electron density in the neutral form, which is more hydrophobic than the cation. Therefore, the removal efficiency of CPFX is higher at pH 9 [16]. So, in the future, the effectiveness of removing CPFX content in wastewater using nZVI, MXene, and nZVI-MXene can be studied with pH 9 conditioning to obtain high adsorption capacity.

4. Conclusion

The point of zero charge (pH_{pzc}) is the pH at which the material's surface is electrically neutral. At a pH less than pH pzc ($pH < pH_{pzc}$), the material's surface will be positively charged and CPFX has a negative ion charge ($CPFX^-$). The material's surface will be negatively charged if the pH is less than pH_{pzc} ($pH > pH_{pzc}$) and CPFX has a positive ion charge ($CPFX^+$). pHpzc on nZVI material is 4.25. The pH_{pzc} of the MXene material is 2.8. The pH pzc value of the MXene material is lower than that of nZVI. This result can be due to the use of HF etching agents during the MXene synthesis process to strengthen the strong acid functional groups, in contrast to nZVI, which is usually produced from Fe reduction and has a more basic surface due to its oxide and hydroxide content. The pH pzc on the nZVI-MXene material is 3.45, which is lower than nZVI but higher than MXene.

This result is due to the presence of acid groups from MXene, which dominate the surface of the material, which can cause the pHpzc value to be closer to the pHpzc value of MXene than nZVI but still higher than MXene due to the influence of the base group from nZVI. In addition to electrostatic interactions, other mechanisms exist during high pH reactions, such as interactions of active functional groups on the material's surface with adsorbates through chemical bonds. There are other factors that cause the highest removal efficiency to occur at pH 9, namely the ionic form of CPFX at each different pH. At pH 5 and 7, CPFX has a weak cation charge. Therefore, the removal efficiency of CPFX is higher at pH 9.

These findings indicate that nZVI-MXene nanocomposites have promising potential as an adsorbent for CPFX removal from wastewater, particularly under pH 9 conditions. The understanding of pH pzc behavior in composite materials can aid in optimizing adsorption processes for pharmaceutical contaminants in aqueous environments. Future studies should explore the long-term stability and regeneration potential of nZVI-MXene adsorbents, as well as their performance in real wastewater conditions. Additionally, further investigations on the synergistic effects of nZVI-MXene with other treatment methods, such as photocatalysis or advanced oxidation process, could enhance its effectiveness in pharmaceutical wastewater treatment.

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6. References

[1] Xu, Y., Gu, Y., Peng, L., Wang, N., Chen, S., Liang, C., Liu, Y., & Ni, B. J. (2023). Unravelling ciprofloxacin removal in a nitrifying moving bed biofilm reactor: Biodegradation mechanisms and pathways. Chemosphere, 320(January), 138099. https://doi.org/10.1016/j.chemosphere.2023.138099

[2] Alshahrani, A. A., Alghamdi, M. D., Alqarni, L. S., Aissa, M. A. Ben, & Modwi, A. (2024). The preparation of Zr-TiO2@g-C3N4 nanocomposites to remove ciprofloxacin from water. Journal of Molecular Structure, 1315(June), 138891. https://doi.org/10.1016/j.molstruc.2024.138891

[3] Khan, P., Saha, R., & Halder, G. (2024). Towards sorptive eradication of pharmaceutical micro-pollutant ciprofloxacin from aquatic environment: A comprehensive review. Science of the Total Environment, 919(February), 170723. https://doi.org/10.1016/j.scitotenv.2024.170723

[4] Sathishkumar, K., Naraginti, S., Lavanya, K., Zhang, F., Ayyamperumal, R., & Liu, X. (2023). Intimate coupling of gC3N4/CdS semiconductor on eco-friendly biocarrier loofah sponge for enhanced detoxification of ciprofloxacin. Environmental Research, https://doi.org/10.1016/j.envres.2023.116558

[5] Kim, D. G., Choi, D., Cheon, S., Ko, S. O., Kang, S., & Oh, S. (2020). Addition of biochar into activated sludge improves removal of antibiotic ciprofloxacin. Journal of Water Process Engineering, 33(August 2019), 101019. https://doi.org/10.1016/j.jwpe.2019.101019

[6] Rosas-Ramírez, J. R., Orozco-Hernández, J. M., Elizalde-Velázquez, G. A., Raldúa, D., Islas-Flores, H., & Gómez-Oliván, L. M. (2022). Teratogenic effects induced by paracetamol, ciprofloxacin, and their mixture on Danio rerio embryos: Oxidative stress implications. Science of the Total Environment, 806. https://doi.org/10.1016/j.scitotenv.2021.150541

[7] Li, S., Li, L., & Zhang, W. (2023). Nanoscale Zero-Valent Iron (nZVI) for Heavy Metal Wastewater Treatment: https://doi.org/10.1016/j.eng.2023.08.012.

[8] Cao, H. (2023). Beyond graphene and boron nitride: why MXene can be used in composite for corrosion protection on metals? Composites Part B: Engineering, 271(September https://doi.org/10.1016/j.compositesb.2023.111168

[9] Li, J., Liu, H., Shi, X., Li, X., Li, W., Guan, E., Lu, T., & Pan, L. (2024). MXene based anode materials for high performance sodium-ion batteries. Journal of Colloid and Interface Science, 658(October 2023), 425–440. https://doi.org/10.1016/j.jcis.2023.12.065

[10] Nugrahani, I., Tjengal, B., Gusdinar, T., Horikawa, A., & Uekusa, H. (2020). A comprehensive study of a new 1.75 hydrate of ciprofloxacin salicylate: SCXRD structure determination, solid characterization, water stability, solubility, and dissolution study. https://doi.org/10.3390/cryst10050349

[11] Higgins, P., Siddiqui, S. H., & Kumar, R. (2022). Design of novel metal hydroxide bio-nanocomposite (CBCS@LDH) for the scavenging of ciprofloxacin (CPN) drug from its aqueous solution: Kinetic, isotherm, thermodynamic and reusability studies. Current Research in Green and Sustainable Chemistry, 5(February), 100298. https://doi.org/10.1016/j.crgsc.2022.100298

[12] Mustafa, R. UI., M., Khurshid, H., & Isa, M. H. (2024). Nanoscale zero-valent iron (NZVI) intercalated MXene (Ti3C2Tx) for removal of polycyclic 92 aromatic hydrocarbons in wastewater. Journal of Environmental Chemical Engineering, 12(2), 112149. https://doi.org/10.1016/j.jece.2024.112149

[13] Chen, C., Luo, W., Xu, J., & Niu, D. (2023). Investigation of the adsorption and degradation of metronidazole residues in agricultural wastewater by nanocomposite based on nZVI on MXene. Alexandria Engineering Journal, 80(June), 41–47. https://doi.org/10.1016/j.aej.2023.08.055

[14] Chen, D., Li, M., Yue, X., Ji, Y., Xu, Y., Pan, J., & Dong, C. (2024). Correlation between pitting susceptibility and surface acidity, point of zero charge of passive film on aluminum: Influence of alloying elements. Corrosion Science, 227(November 2023).

[15] Aafria, S., Batra, B., Lamba, P., Yadav, S., Rana, J. S., & Sharma, M. (2023). Efficient removal of synthetic dye by employing H2O2/nZVI-rGO nanocomposite system. Environmental Nanotechnology, Monitoring and Management, 20(February), https://doi.org/10.1016/j.enmm.2023.100808

[16] Ge, X., Meng, G., & Liu, B. (2022). Ultrasound-assisted preparation of LaFeO3/polystyrene for efficient photo-Fenton degradation of ciprofloxacin hydrochloride. Journal of Industrial and Engineering Chemistry, 115, 390 401. https://doi.org/10.1016/j.jiec.2022.08.023