OPTIMIZING PHOSPHATE REMOVAL BY MANIPULATING MANGANESE AND COBALT LEVELS IN SOIL AQUIFER TREATMENT SYSTEM

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Abstract

Manganese (Mn^{2+}) and cobalt (Co^{2+}) metals have been reported to exhibit complex interactions with phosphate (PO_4^{3-}) ions, which can influence their mobility, reactivity, and removal behavior in soil aquifer treatment system (SAT). This study aimed to investigate the role of manganese (Mn^{2+}) and cobalt (Co^{2+}) in phosphate (PO_4^{3-}) removal within a soil aquifer treatment system. A lab-scale column experiment was conducted using sand as the filtration media, and a synthetic wastewater containing 20 mg/L PO_4^{3-}, 60 mg/L Mn^{2+}, and 40 mg/L Co^{2+} was used. The breakthrough curves showed efficient removal of PO_4^{3-} during the infiltration process, with concentrations reaching as low as 1 mg/L. The regression analysis revealed that Mn^{2+} had a strong negative correlation effect on PO_4^{3-} concentration, indicating its stimulatory role in PO_4^{3-} removal. Conversely, Co^{2+} showed a strong positive correlation effect, suggesting its promoting effect on PO_4^{3-} concentration. Optimization analysis identified optimal concentrations of 57.4 mg/L for Mn^{2+} and 4.8 mg/L for Co^{2+} that interacted with lower PO_4^{3-} concentrations, achieving the desired outcome of reducing PO_4^{3-} levels. These findings highlight the importance of considering Mn^{2+} and Co^{2+} concentrations in soil aquifer treatment systems for effective phosphate removal.

Keywords: *Soil aquifer treatment. Phosphate. Manganese. Cobalt.*

1. Introduction

Phosphorus is an essential nutrient for plant growth and is commonly found in wastewater effluents from various sources, including domestic, agricultural, and industrial activities (Fadiran et al., 2008). However, the discharge of phosphate-rich wastewater into natural water bodies can lead to eutrophication, causing significant ecological imbalances and threatening water quality (Ayele and

Atlabachew, 2021). To address this environmental challenge, effective wastewater treatment technologies are needed to remove phosphate and prevent its detrimental effects on aquatic ecosystems (Chowdhary et al., 2020).

Soil aquifer treatment (SAT) has emerged as a promising and sustainable technology for wastewater treatment and reuse (Sharma and Kennedy, 2017). It involves the infiltration of wastewater through a porous soil medium, followed by natural biological, physical, and chemical processes that remove contaminants and promote the natural purification of water (Bali and Gueddari, 2019). SAT systems harness the inherent capacity of soil and aquifer layers to filter, adsorb, and transform pollutants, including phosphates, thereby reducing their concentration in the treated effluent (Gharbia et al., 2016). The efficient removal of phosphate is critical in SAT systems to ensure the production of high-quality treated water suitable for various applications, such as agricultural irrigation, groundwater recharge, and ecosystem preservation. Numerous factors influence phosphate removal in SAT systems, including hydraulic and physicochemical parameters, microbial activity, and the composition of the infiltrating wastewater (Pavelic et al., 2011).

In soil aquifer treatment (SAT) systems, the removal of phosphate (PO_4^{3-}) is facilitated by various mechanisms. Firstly, adsorption plays a crucial role, where soil minerals like iron and aluminum oxides, clay minerals, and organic matter possess a high affinity for PO_4^{3-} ions, attracting and retaining them on their surfaces (Gharbia et al., 2022). Precipitation is another important mechanism, occurring when PO_4^{3-} ions react with cations such as calcium or iron to form insoluble phosphate compounds (Hanyabui et al., 2020). Ion exchange is facilitated by the cation exchange capacity of soil particles, particularly clay minerals, enabling the exchange of PO_4^{3-} ions with other ions present in the soil matrix (Malovanyy et al., 2019). Biological processes also contribute to PO_4^{3-} removal as microorganisms assimilate and metabolize PO_4^{3-} as a nutrient source (Atta et al., 2020). Filtration through the soil media physically traps and retains larger particles, including particulate forms of PO_4^{3-}. Redox reactions, particularly in anaerobic zones, lead to the precipitation of iron and manganese phosphates, aiding in PO_4^{3-} removal (Zhang et al., 2023). Vegetation uptake further enhances PO_4^{3-} removal by plants and their root systems (Jacklin et al., 2022). The relative importance of these mechanisms varies based on soil properties, wastewater characteristics, hydraulic conditions, and system design. The synergistic action of these processes in SAT systems ensures the efficient removal of PO_4^{3-}, contributing to the treatment and remediation of wastewater and the protection of water resources and ecosystems. However, recent studies have highlighted the potential role of heavy metals, particularly manganese (Mn^{2+}) and cobalt (Co^{2+}), in modulating phosphate removal performance.

Manganese and cobalt are naturally occurring trace elements found in soil and groundwater, and they can exist in varying concentrations depending on geological and environmental factors (Sappa et al., 2020). These metals have been reported to exhibit complex interactions with phosphate ions, which can influence their mobility, reactivity, and removal behavior in SAT systems. Interestingly, the effect of manganese and cobalt on phosphate removal is not straightforward, as their impact can vary depending on their concentration, speciation, and the prevailing environmental conditions (Bhat et al., 2018). Several studies have explored the role of manganese and cobalt in phosphate removal, but the findings are often inconsistent and context-specific. Some studies have reported the stimulatory effect of manganese on phosphate removal, suggesting that it can enhance the adsorption and precipitation of phosphate compounds, leading to improved removal efficiency (Barrioni et al., 2019). On the other hand, cobalt has been found to have inhibitory effects on phosphate removal in certain conditions, potentially due to its interference with the adsorption and transformation processes (Qi et al., 2014). Understanding the interplay between manganese, cobalt, and phosphate removal is crucial for

optimizing the performance of SAT systems and enhancing their efficiency in phosphate removal. By manipulating the levels of manganese and cobalt, it is possible to modulate their influence on phosphate removal and identify the optimal conditions for maximizing phosphate removal efficiency. This knowledge can inform the design and operation of SAT systems, allowing for the development of more sustainable and effective approaches for phosphate removal in wastewater treatment.

Therefore, the primary objective of this study is to investigate the role of manganese and cobalt as stimulants or inhibitors in phosphate removal within soil aquifer treatment systems. Specifically, we aim to evaluate the effect of varying concentrations of manganese and cobalt on phosphate removal efficiency and elucidate the underlying mechanisms involved. Through comprehensive laboratory-scale experiments and rigorous data analysis, we will assess the impact of different metal concentrations on phosphate adsorption, precipitation, and overall removal performance.

2. Materials and methods

A lab-scale column packed with sand soil was used as the filtration media to simulate the soil aquifer treatment system. A peristaltic pump was employed to control a constant and slow infiltration rate of 0.2 mL/min. Synthetic wastewater was prepared, containing PO_4^{3-} with a concentration of 20 mg/L, Mn^{2+} with a concentration of 60 mg/L, and Co^{2+} with a concentration of 40 mg/L. These specific concentrations were selected in accordance with the guidelines outlined in the (van Loosdrecht et al., 2016), which comprehensively details the compositions of wastewater typically encountered in laboratory settings. The components for the synthetic wastewater, including KH_2PO_4, $MnSO_4 \cdot 4H_2O$, and $CoCl_2 \cdot 6H_2O$, were used to achieve the desired concentrations. Samples from the experimental setup were collected and analyzed for their PO_4^{3-}, Mn^{2+}, and Co^{2+} concentrations. The PO_4^{3-} concentration was measured using a HACH direct-reading spectrophotometer (DR2000), while the Mn^{2+} and Co^{2+} concentrations were determined using a plasma atomic emission spectroscopy device. To explore the role and relationship between the PO_4^{3-} concentration and the Mn^{2+} and Co^{2+} concentrations, a regression model was employed. This model allowed for the assessment of the influence of Mn^{2+} and Co^{2+} on PO_4^{3-} removal efficiency. Furthermore, an optimization matrix was applied to identify the optimal concentrations of Mn^{2+} and Co^{2+} that could interact with lower PO_4^{3-} concentrations. This optimization approach aimed to determine the most effective combination of Mn^{2+} and Co^{2+} concentrations that would enhance the removal of PO_4^{3-} from the wastewater. By evaluating different combinations and analyzing their effects on PO_4^{3-} removal, the study sought to identify the optimal conditions for achieving maximum efficiency in removing PO_4^{3-} using Mn^{2+} and Co^{2+} as potential stimulants or inhibitors. Overall, this experimental setup and analytical approach provided a systematic framework for investigating the role of Mn^{2+} and Co^{2+} in the removal of PO_4^{3-} and determining their optimal concentrations for enhanced performance in soil aquifer treatment system.

3. Results and discussions

In the column experiment, breakthrough curves (BTCs) were generated to monitor the behavior of PO_4^{3-}, Mn^{2+}, and Co^{2+} over time. Figure 1 illustrates the BTCs for these species. The BTC for PO_4^{3-} demonstrated efficient removal during the initial stages of infiltration through the sand media column, with the concentration increasing to 20 mg/L within the first day. However, over the subsequent 4 days, the concentration gradually decreased and stabilized at around 1 mg/L. Throughout the experiment, the PO_4^{3-} concentration exhibited fluctuations, with both increases and decreases. Towards the end of the 5-day experiment, there was a notable spike in the PO_4^{3-} concentration, reaching 15 mg/L, and ultimately

returning to 20 mg/L. This sudden increase suggests the occurrence of column exhaustion and clogging, affecting the overall removal efficiency of PO_4^{3-}.

In contrast, the BTCs for Mn^{2+} and Co^{2+} displayed different patterns. The concentrations of Mn^{2+} and Co^{2+} in the output samples reached their initial concentrations of 60 mg/L and 40 mg/L, respectively, within approximately 1.5 days. These concentrations remained relatively stable throughout the remainder of the experiment. The consistent concentrations of Mn^{2+} and Co^{2+} imply that their removal efficiencies were not as prominent as that of PO_4^{3-}. The stable concentrations indicate that Mn^{2+} and Co^{2+} may have reached an equilibrium state with the sand media, resulting in limited further removal.
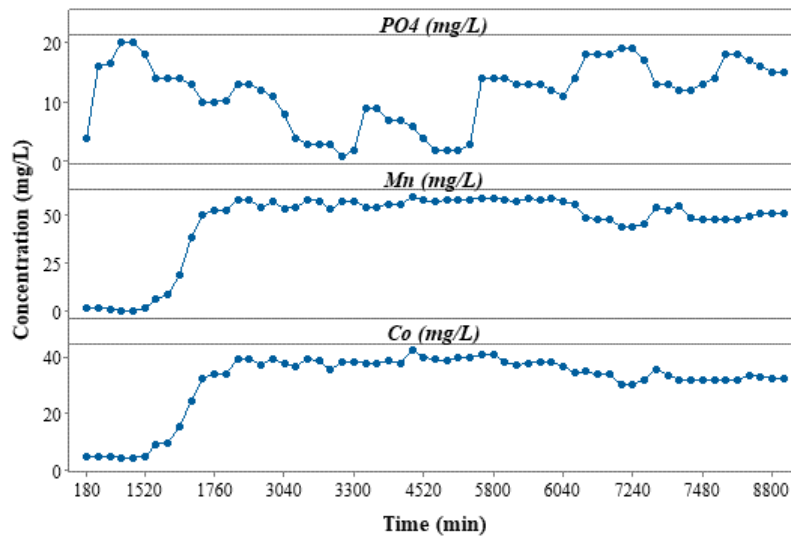

Figure 1. *Breakthrough curves for PO_4^{3-}, Mn^{2+}, and Co^{2+} concentrations over time during SAT system*

These findings from the BTC analysis provide valuable insights into the behavior of PO_4^{3-}, Mn^{2+}, and Co^{2+} within the soil aquifer treatment system. The efficient removal of PO_4^{3-} during the early stages of infiltration highlights its susceptibility to the sand media column. The fluctuations observed in the PO_4^{3-} concentration, along with the subsequent jump towards the end of the experiment, indicate the influence of column exhaustion and clogging on its removal. On the other hand, Mn^{2+} and Co^{2+} showed relatively stable concentrations, suggesting a reduced removal capacity compared to PO_4^{3-}. Further investigation is warranted to better understand the interactions between Mn^{2+}, Co^{2+}, and PO_4^{3-} in soil aquifer treatment systems and optimize their removal efficiency.

The linear regression model was utilized to analyze and simulate the relationship and interaction between PO_4^{3-} and Mn^{2+}, as well as between PO_4^{3-} and Co^{2+}, in terms of their performance in the soil aquifer treatment system. The statistical parameters, namely the p-value and variance inflation factor (VIF), were employed to evaluate the significance of these relationships.

For the regression model between PO_4^{3-} and Mn^{2+}, a p-value of 0.013 was obtained. The p-value represents the probability of observing a relationship between the variables by chance. In this case, the low p-value indicates a statistically significant relationship between PO_4^{3-} and Mn^{2+}. Additionally, the VIF value of 190.44 suggests that there may be collinearity present between these variables. Collinearity refers to the correlation between independent variables, which can affect the accuracy and interpretation of the regression model. Similarly, the regression model between PO_4^{3-} and Co^{2+} yielded a p-value of 0.045, indicating a statistically significant relationship between these variables. The VIF value of 215.40

suggests the presence of collinearity between PO_4^{3-} and Co^{2+}. These statistical parameters provide insights into the significance and strength of the relationships between PO_4^{3-} and Mn^{2+}, as well as between PO_4^{3-} and Co^{2+}. The low p-values indicate that the relationships are unlikely to occur by chance, implying a genuine association between these variables. However, the high VIF values suggest the presence of collinearity, which can complicate the interpretation of the individual effects of PO_4^{3-}, Mn^{2+}, and Co^{2+}.

The linear factorial regression model revealed important insights into the correlation effects of Mn^{2+} and Co^{2+} on the removal of PO_4^{3-} as shown in figure 2, which presents the distribution of the experimental results for the PO_4^{3-} concentration according to Mn^{2+} and Co^{2+} concentration also, the linear factorial regression model which models the relationship behavior between PO_4^{3-} with Mn^{2+} and Co^{2+} in a linear fitted curve. The R-square for the model to the experimental data reached 97.4%, reflecting the model's high accuracy.
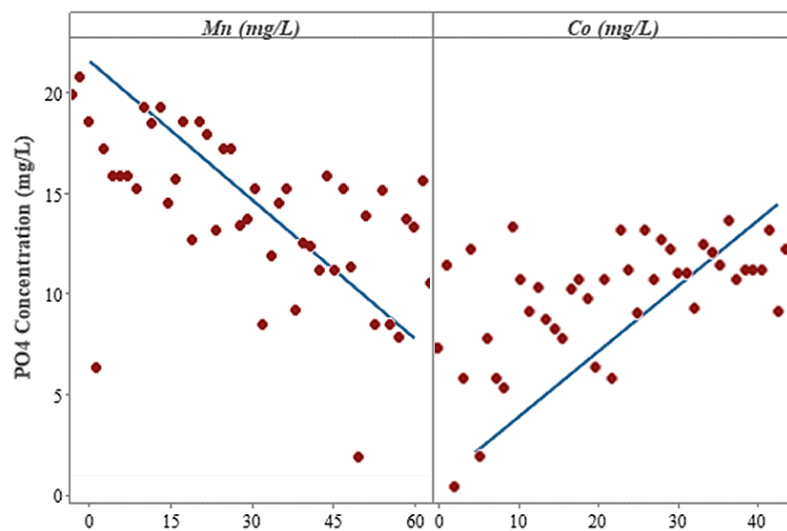

Figure 2. *Factorial linear regression model for the relationship between PO_4^{3-} concentration with Mn^{2+} and Co^{2+} concentrations*

The results indicate that Mn^{2+} has a strong and high negative correlation effect on PO_4^{3-} removal. This means that as the concentration of Mn^{2+} increases, the concentration of PO_4^{3-} decreases. The negative correlation suggests that Mn^{2+} has an inhibitory effect on the concentration of PO_4^{3-} in the soil aquifer treatment system, potentially hindering its accumulation. On the other hand, the analysis showed that Co^{2+} has a strong and high positive correlation effect on PO_4^{3-} concentration. This implies that as the concentration of Co^{2+} increases, the concentration of PO_4^{3-} also increases. The positive correlation suggests that Co^{2+} has a promoting effect on the concentration of PO_4^{3-}, potentially enhancing its accumulation.

The oxidizing power of Mn^{2+} can lead to the oxidation of organic matter, which releases bound PO_4^{3-} and makes it available for adsorption onto sand surfaces or uptake by microorganisms (Buamah, 2009). This process is known as microbially mediated PO_4^{3-} release and is facilitated by Mn-oxidizing bacteria. Therefore, the presence of Mn^{2+} in the sand column can enhance PO_4^{3-} removal. Also, under oxic conditions, Mn^{2+} can form solid manganese oxides/hydroxides that can adsorb PO_4^{3-} ions, leading to decreased PO_4^{3-} concentration in the solution. Mn^{2+} can also promote the growth of microorganisms that

can participate in PO_4^{3-} removal through biological processes, such as microbial assimilation or microbial conversion of PO_4^{3-} to less soluble forms (Granger, 2013). On the other hand, the impact of Co^{2+} on PO_4^{3-} removal can be more complex and dependent on the pH and redox conditions in the sand column. At low pH, Co^{2+} can form a soluble Co-PO4 complex, which reduces the amount of PO_4^{3-} available for adsorption onto the sand surface or uptake by microorganisms (Hawco et al., 2016). This reduces the efficiency of PO_4^{3-} removal. However, at higher pH, Co^{2+} can form $Co(OH)_2$, which can adsorb PO_4^{3-} and enhance its removal. Additionally, Co^{2+} can also act as a trace element that promotes microbial activity and improve PO_4^{3-} removal (Chaurasia et al., 2021). Therefore, the impact of Co^{2+} on PO_4^{3-} removal can be dependent on various factors, including pH, redox conditions, and microbial activity. However, Co^{2+} can have a positive impact on PO_4^{3-} reduction by promoting the growth of phosphate-accumulating organisms that can take up PO_4^{3-} from the solution and store it in their cells as polyphosphate (Mañas et al., 2011). This process, known as enhanced biological phosphorus removal, can effectively remove PO_4^{3-} from wastewater. Co^{2+} can also form precipitates with PO_4^{3-}, leading to decreased PO_4^{3-} concentration in the solution (Manas, 2011). However, it's important to note that the impact of Mn^{2+} and Co^{2+} on PO_4^{3-} removal can depend on various factors, such as the concentration and speciation of the metals, the presence of other contaminants, and the properties of the soil or sediment. The specific mechanisms involved in Mn^{2+} and Co^{2+} influence on PO_4^{3-} removal may also vary depending on the conditions of the system.

The optimization matrix analysis aimed to determine the optimal concentrations of Mn^{2+} and Co^{2+} that would interact with lower concentrations of PO_4^{3-} as shown in figure 3. The results revealed that at a concentration of 57.4 mg/L for Mn^{2+} and 4.8 mg/L for Co^{2+}, the lowest value of PO_4^{3-} concentration was achieved, approaching approximately 1 mg/L.
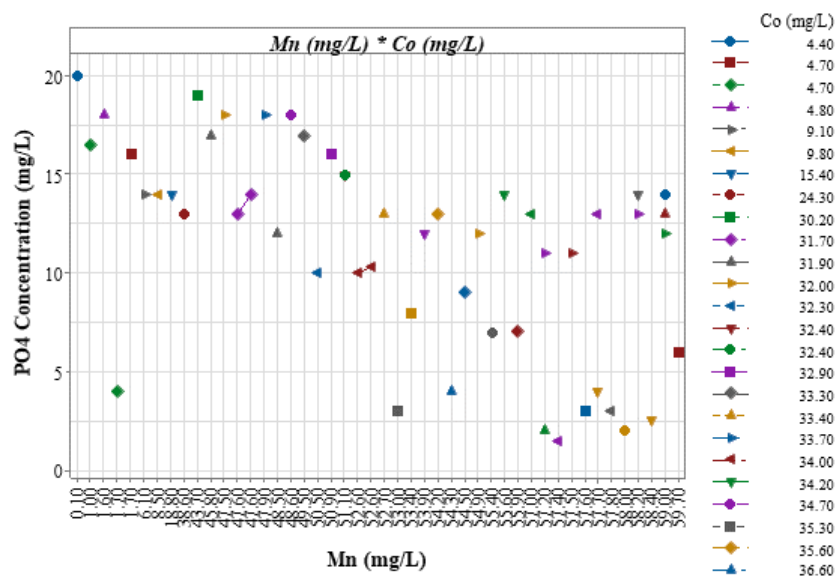

Figure 3. *Optimization matrix for PO_4^{3-} concentration with Mn^{2+} and Co^{2+} concentration interactions*

This finding suggests that the presence of Mn^{2+} and Co^{2+} at these specific concentrations has an inhibitory effect on the concentration of PO_4^{3-}. By optimizing the concentrations of Mn^{2+} and Co^{2+}, it is possible to minimize the concentration of PO_4^{3-} in the soil aquifer treatment system. These results have important implications for the design and management of soil aquifer treatment systems aiming to

remove PO_4^{3-}. By carefully controlling and optimizing the concentrations of Mn^{2+} and Co^{2+} within the system, it is possible to achieve lower levels of PO_4^{3-} concentration. This is particularly significant as high concentrations of PO_4^{3-} can contribute to water pollution and environmental degradation.

The changing concentrations of Mn^{2+} and Co^{2+} in synthetic wastewater can potentially influence the performance of PO_4^{3-} treatment, as presented in the optimization matrix in figure 3, beyond just chemical reactions and biological activity. These changes can impact the speciation and reactivity of phosphate ions. For instance, if the concentrations of Mn^{2+} and Co^{2+} are altered, it could form metal-phosphate complexes or affect the solubility of phosphate compounds. The presence of different metal ions can influence the growth and activity of microorganisms. Some microorganisms are sensitive to metal toxicity, and changes in metal concentrations can impact microbial communities and their performance in breaking down organic matter and removing nutrients. Additionally, specific metal ions can serve as essential cofactors for microbial enzymes involved in biodegradation, which in turn could affect its removal efficiency during treatment processes. Therefore, the variations in Mn^{2+} and Co^{2+} concentrations may directly impact the chemical and biological interactions involving phosphate, potentially altering its behavior and removal mechanisms during treatment.

4. Conclusion

The impact of Mn^{2+} and Co^{2+} on PO_4^{3-} removal in sand columns under oxic conditions in soil aquifer treatment system can be complex and dependent on various factors, such as the concentration of the metals and the characteristics of the sand. Generally, Mn^{2+} can have a positive impact on PO_4^{3-} removal percentage due to its ability to act as an electron acceptor and promote microbial activity as a powerful oxidizer. Co^{2+}, on the other hand, can have a negative impact on PO_4^{3-} removal percentage by forming a soluble $Co-PO_4$ complex, which reduces the amount of PO_4^{3-} available for adsorption onto the sand surface or uptake by microorganisms. However, the exact mechanisms and factors that determine the impact of these metals on PO_4^{3-} removal are still the subject of ongoing research. The optimization matrix analysis identified optimal concentrations of 57.4 mg/L for Mn^{2+} and 4.8 mg/L for Co^{2+} that interacted with lower PO_4^{3-} concentrations, achieving the desired outcome of reducing PO_4^{3-} levels. These findings demonstrate the importance of considering the concentrations of Mn^{2+} and Co^{2+} in soil aquifer treatment systems for effective phosphate removal. By optimizing the concentrations of these metals, it is possible to minimize PO_4^{3-} concentrations, thereby mitigating the risk of water pollution and environmental degradation. However, further research is needed to validate these findings and understand the underlying mechanisms of the inhibitory and promoting effects.

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