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Functionalization of Iron Nanoparticles with Linkers for Removal of Pollutants in Water

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Abstract

Today, quality monitoring of water resources played an influential role in its exploitation and use. Water sources usually contain heavy metals in minor concentrations. The research showed various methods of removing heavy metals in aqueous solutions, such as chemical reduction, ion exchange, adsorption, etc. Hence, the widespread applications of nanotechnology to remove toxic pollutants from different contaminated water sources are known. In this study, while the existence of other methods for pollutants elimination from water, the use of iron nanoparticles was investigated. Eco-friendly and cost-effective nanomaterials are vital to ultimately removing contaminants from water. Meanwhile, iron nanoparticles are available, cheap, and practical in water and wastewater treatment. Therefore, Nano Zero-Valeant Iron (nZVI) with high surface area, nanoscale particle size, unique catalytic activity, more reactivity than bulk iron, and mobility in the underground has attracted significant consideration due to their performance in removing pollutants from aqueous solutions. Since nZVI could have aggregated, various linkers have been used to stabilize these particles on the substrate, and the use of some linkers to support these nanoparticles was examined. The results showed that hydrophilic and biodegradable linkers such as Starch, Carboxymethyl cellulose (CMC), Polyethylene glycol (PEG), Polyacrylamide (PAM), and Polyvinylpyrrolidone (PVP) could increase the speed of chemical reaction in reducing pollutants from water. Because linkers often had different functional groups that could enhance the stabilizing of these particles on the substrate. Among these linkers, PVP, as a hydrophilic, cheap, and biodegradable polymer, has performed an excellent function in supporting nZVI.

Keywords: Heavy metals, Linker, Pollution, Water, Zero-valent iron nanoparticles.

1. Introduction

The quality of water resources has long been a matter of concern for humanity, and ensuring access to clean drinking water has become a critical issue in all aspects of human life (Najafabadi et al., 2018, Connolly et al., 2020; Fida et al., 2022). Therefore, it is essential to remove pollutants, especially heavy metals, from water sources to safeguard human health. Heavy metal contamination primarily arises from mining activities and human interventions, while inadequate urban and industrial waste treatment methods have also contributed to introducing heavy metals into water (Ozaki et al., 2019; Warren-Vega et al., 2023)

Numerous techniques are available for reducing and eliminating contaminants from water sources. Among these, iron nanoparticles, which possess high surface areas and particle sizes in the nanoscale range, are widely recognized as excellent materials with a remarkable absorption capacity (Barzegar et al., 2018; Brasili, et al., 2020; Yahyaeian et al., 2023). Simultaneously, the depletion of petroleum resources and growing environmental concerns, such as global warming, have generated significant interest in developing sustainable ecological materials for mitigating water pollutants (Habibi, 2014; Mohamed et al., 2023). Given that zero-valent iron nanoparticles are prone to aggregation, different linkers such as starch (Kumari and Duetta, 2020), cellulose (Li et al., 2018), polyethylene glycol (PEG) (Wu et al., 2020), polyacrylamide (PAM) (Li et al., 2021), and Polyvinylpyrrolidone (PVP) (Chen et al., 2019) are employed to augment the efficiency of these particles as absorbers in water. These stabilizers prevent the agglomeration of zero-valent iron nanoparticles through beneficial bonds, thus increasing the reactivity of these nanoparticles as absorbers in contaminated water (Sidorenko et al., 2022; Liu et al., 2023).

Starch is an appropriate substance among organic, environmentally friendly, and stable organic biopolymers due to its biodegradability, cost-effectiveness, and non-toxicity (Nasrollahzadeh et al., 2021). Research conducted by Kumari and Duetta (2020) demonstrated that starch-enriched zero-valent iron nanoparticles could improve the water chromium removal through advanced oxidation techniques (Kumari and Duetta, 2020). Carboxymethyl cellulose (CMC) is also an anionic polyelectrolyte that can effectively reduce the aggregation of iron nanoparticles at the surface and enhance the mobility of zero-valent iron nanoparticles in porous media (Yu et al., 2020; Liu et al., 2023). Consequently, Xu et al. (2020) discovered that zero-valent iron nanoparticles supported by carboxymethyl cellulose could reduce over 99% of trichloroethene in water within five hours.

Biodegradable surfactants like PEG can also enhance the physical stability of zero-valent iron nanoparticles and reduce their environmental risk (Wu et al., 2020). Jiao et al. (2012) synthesized a new composite of zero-valent iron nanoparticles linked to polyethylene glycol and stabilized on activated carbon, introducing it as an effective catalyst for removing hexavalent chromium. Polyacrylamide (PAM) has been used as a polyelectrolyte to prevent agglomeration and facilitate the transportation of water and soil (Wang et al., 2015). Liu et al. (2021) discovered that PAM, which supports zero-valent iron nanoparticles, can be an effective flocculant. This facilitates the agglomeration of these nanoparticles in water and wastewater treatment while reducing the presence of divalent lead in water. Polyvinylpyrrolidone (PVP) is a nonionic linker that enhances the dispersion of zero-valent iron nanoparticles. This stabilizer is inexpensive, water-friendly, environmentally compatible, and conductive (Tian et al., 2020).

Shamshirgaran et al. (2022) demonstrated that water-compatible biochar, enriched with zero-valent iron nanoparticles and stabilized by Polyvinylpyrrolidone, could significantly reduce hexavalent chromium in groundwater (achieving a reduction rate of 99.6% in only 5 minutes). The current investigation not only examines methods for eliminating contaminants from water but also explores the application of nanotechnology in water treatment. Specifically, the research focuses on the use of zero-valent iron nanoparticles in reducing water contaminants facilitated by various linkers.

2. Methods for removing pollutants from water sources

Various and abundant organic and inorganic compounds are produced in chemical industries, many of which are persistent, toxic, and non-degradable. Removing these compounds from industrial wastewater, groundwater, and natural soil poses a challenging task, mainly when they spread into the environment (Pasinszki and Krebsz, 2020; Romeh, 2023).

As depicted in Fig.1, there exist numerous methods to eliminate contaminants, including heavy metals found in aqueous solutions, such as adsorption, ion exchange, chemical precipitation, membrane filtration, redox processes, electrodialysis, electrolytic extraction, etc. (Zhu et al., 2016). Among these, the adsorption technique is the most common and cost-effective technology for removing heavy metals from water, employing both natural and bio-adsorbents (Chakraborty et al., 2022; Ohale et al., 2023).

Ion exchange is a reversible exchange way between an insoluble solid phase and a liquid phase. The solid phase in the ion exchange procedure can be a crystalline network or gel. If the exchanged ions are positive, it is named a cation exchange; if the ionic species have a negative charge, it is considered an anion exchange. Using a cation exchange method, cations such as Ca^{2+}, Mg^{2+}, Ba^{2+}, Sr^{2+}, and Ra^{2+} can be picked up from an aqueous media. So, Ion exchange is capable of selectively removing heavy metals of high quality. Also, anions such as F^-, AsO_3^{2-}, NO_3^{2-}, SeO_3^{2-}, CrO_4^{2-}, etc. can be removed by an anion exchange method. Although, this technique is utilized in different fields, including water treatment, medical research, mining, agriculture, etc., it cannot be applied on a large-scale duo to its high cost (Stenina et al., 2020; Kordbacheh et al., 2023).

The chemical precipitation method is a process that relies on the reaction between heavy metal ions and a suitable compound to facilitate the sedimentation of the resulting residue from the solution. This method operates on generating insoluble metal precipitates (Peng and Guo, 2020).

Fig. 1. Different methods for reducing pollutants in water (Shrestha et al., 2021)

Nevertheless, the production of sludge, the relatively weak sedimentation of metals, and the environmental impacts of sludge disposal are among the drawbacks of this process (Siti et al., 2013; Saleh et al., 2022). Filtration is a process in which membranes with pore sizes ranging from 0.001 to 0.1 micrometers are used to separate high molecular weight, polymeric, and colloidal contaminants. This process, conducted under pressure, is affected by the electrical load and the surface chemistry of the membrane (Almasian et al., 2018; Elsaid et al., 2023).

In an electrochemical system, oxidation occurs at the anode (the positive side), where electrons are transferred to the cathode (the negative side), and reduction occurs. These two chemical reactions, called redox (reduction-oxidation) reactions, lead to water purification through metal removal. However, this method is costly for industrial applications (Qasem et al., 2021). Electrodialysis is also used to separate ions, considering the difference in electrical potential. This method employs a series of cation exchange and anion exchange membranes that are alternately arranged in parallel to separate ionic salts. The notable purification of water without any chemical reactions or interference is one of the advantages of this method. However, the high cost of the membranes and the challenges in creating an electrical potential remain significant obstacles (Al-Amshawee et al., 2020).

3. Application of zero-valent iron nanoparticles in water treatment

The rapid advancement of nanoscale science and engineering has created unprecedented opportunities for expanding cost-effective and environmentally friendly water purification methods. Among these, nanoparticles, due to their unique properties, are used for various remediation applications. The diverse applications of nanoparticles span various domains, such as heavy metal pollution mitigation, reduction of wastewater pollutant loads, treatment of hydrocarbons, management of solid waste, and handling of radioactive materials, among others (Ajith et al., 2021; Devi et al., 2023).

Among the different nanoparticles used for heavy metal removal, zero-valent iron nanoparticles, due to their minimal particle size, high surface area, and high reactivity, are among the most effective technologies for reducing pollutants in water. These nanoparticles are distinguished as a potent reductive agent and a significant adsorbent in water purification processes (Fu et al., 2014). Consequently, in recent years, zero-valent iron-based catalysts have emerged as an eco-friendly solution for reducing heavy metals from water bodies. These nanoparticles have attracted considerable attention due to their non-toxic nature and easy recyclability using an external magnetic field (Lei et al., 2018 and Hemmat et al., 2021).

Zhu et al. (2017) found that iron zero-valent nanoparticles, when supported on biochar, could decrease hexavalent chromium in water by over 60%. In 2019, research was conducted on the water purification from pollutants such as nickel (II) and copper (II). The findings indicated that zero-valent iron nanoparticles were effective in reducing divalent copper and nickel within a relatively short period (Lou et al., 2019).

Shad et al. (2020) concluded from their research that zero-valent iron nanoparticles, within 24 hours, were able to decrease the phosphate, ammonia, nitrate, lead, and chloride in water by 99.51%, 88.01%, 86.33%, 79.33%, and 83.04% respectively. Zafar et al. (2021) explored the impact of zero-valent iron nanoparticles on contaminated waters. In their case study, they reported a reduction in tetrachloroethylene and trichloroethylene concentrations in groundwater between 50% and 97% over three months.

4. Linkers for stabilizing zero-valent iron nanoparticles.

Organic and inorganic linkers can alter the properties of zero-valent iron nanoparticles.

4.1. Starch

Starch, as a biodegradable and renewable raw material, provides enhanced stability to zero-valent iron nanoparticles. It also serves as a natural linker, abundant in hydroxyl groups, with a strong bond with various functional groups (Nasrollahzadeh et al., 2021).

Malekzadeh et al. (2018) conducted a study that showed the adsorption behavior of naphthalene on a sorbent comprising starch-modified zero-valent iron nanoparticles. The results indicated that the adsorption process followed a monolayer mechanism and conformed to the Langmuir adsorption model. In addition, the maximum adsorption capacity could be calculated as 24.752 milligrams per gram. The reaction time (five minutes) is also preferable for naphthalene adsorption compared to other adsorbents (Malekzadeh et al., 2018).

Elkady et al. (2019) conducted a study on synthesizing a nanocomposite consisting of starch-linked zero-valent iron. Their research revealed that the incorporation of starch facilitated the dispersion and stabilization of zero-valent iron nanoparticles while preserving their crystal structure characteristics. Furthermore, adding this linker demonstrated the ability to reduce aggregation, enhance distribution, and improve reactivity, resulting in increased efficiency of zero-valent iron nanoparticles to reduce Acid Blue color in water sources (Elkady et al., 2019).

In one research, it was demonstrated that zero-valent iron nanoparticles enriched with potato starch, employed as a stabilizer, could significantly enhance chromium removal from water. SEM (Scanning Electron Microscope) analysis indicated that starch has a multiplicative, positive impact on supporting zero-valent iron nanoparticles. It formed a layer of polymeric molecules on the surface, generating potent spatial repulsive forces. Consequently, the amplified surface charge of the nanoparticles resulted in the electrostatic stabilization of a uniform dispersion and a reduction in particle size (Kumari and Duetta, 2020).

Yang et al. (2021) synthesized a new composite featuring zero-valent iron nanoparticles stabilized on biochar and supported by enduring starch (Fig. 2). They demonstrated remarkable performance in reducing hexavalent chromium in water (reduction percentage = 99.67%). The results from fitting kinetic models in this study showed that the maximum adsorption capacity of hexavalent chromium by the composite containing zero-valent iron and starch is 122.86 mg/g (Table 1).

4.2. Cellulose

Cellulose, identified by the formula $(C_6H_{10}O_5)_n$, is the most plentiful organic polymer on Earth. Essentially, it is a polysaccharide comprising thousands of interconnected glucose units (Li et al., 2018). According to a study by Zhang et al. (2019), zero-valent iron nanoparticles anchored on biochar and supported by carboxymethyl cellulose could thoroughly eradicate 100 mg/L of hexavalent chromium from water solutions within 18 hours. In another study by Zhao et al. (2019), sulfided zero-valent iron nanoparticles were synthesized, supported by carboxymethyl cellulose.

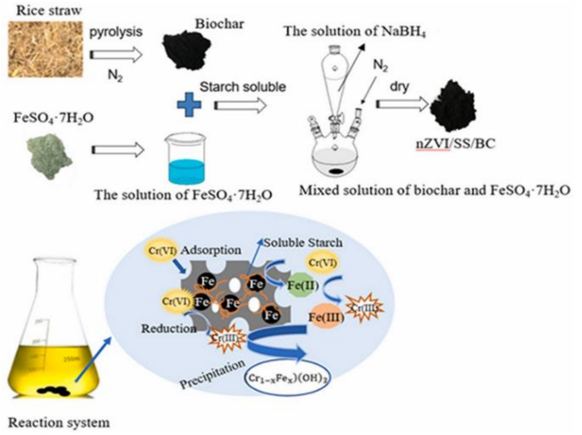

Fig. 2. A depiction of the synthesis and application of zero-valent iron nanoparticles stabilized on biochar and modified with starch for reducing hexavalent chromium in water (Yang et al., 2021).

Table 1. Some starch nanomaterial-based Fe^0 to removing pollutants in water

Materials	Contaminant	pH	The catalyst dosage. (g/l)	Initial contaminant Conc.(mg/l)	Time of reaction	Removal rate
SnZVI particles	Nitrate	5.0	1	100	480min	----
Starch-modified Fe^0 nanoparticle	Naphthalene	5.0	1	5	5min	>99%
S-nZVI@AC	Chromium (VI)	5.0	0.6	10	----	99.96%
Fe^0 st	Acid Blue 25 (dye)	7.0	0.5	600	6min	>99.9%
S-nZVI	Chromium (VI)	3.0	0.5	50	180min	>70%
nZVI/SS/BC600	Chromium (VI)	2.0	1	50	----	99.67 %

Various tests showed that the cellulose-containing catalyst demonstrated superior performance in removing hexavalent chromium in groundwater over a similar time (removal efficiency = 535 mg/g at an initial concentration of 50 mg/L of hexavalent chromium) (Zhao et al., 2019).

The research conducted by Xu et al. (2020) illustrated the polymeric stabilization of zero-valent iron nanoparticles using cellulose. Cellulose could enhance the sub-surface transport of zero-valent iron on a nanoscale, thus increasing the utilization efficiency of electrons.

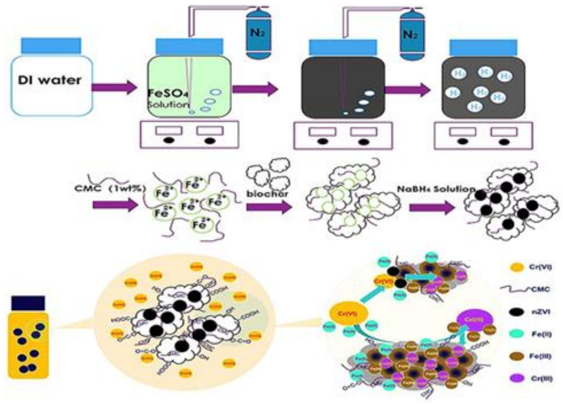

Fig. 3. Mechanism of chromium removal using zero-valent iron nanoparticles anchored on biochar and supported by carboxymethyl cellulose (Zhang et al., 2019).

Furthermore, they investigated the use of sulfided zero-valent iron nanoparticles stabilized with carboxymethyl cellulose to reduce trichloroethylene contaminants in water and achieved commendable results (Xu et al., 2020).

Additionally, Zhao et al. (2022) discovered that zero-valent iron nanoparticles, supported by carboxymethyl cellulose due to their unique crystalline structure and particle size, exhibit high efficiency and capacity to remove Vanadium (V) and Chromium (VI) from water (Table 2).

Table 2. Some nZVI supported by cellulose to remove pollutants in water

Materials	Contaminant	pH	The catalyst dosage. (g/l)	Initial contaminant Conc.(mg/l)	Time of reaction	Removal efficiency or capacity	Ref.
Microcrystalline cellulose immobilized nZVI (CI-2)	Chromium (VI)	3.0	0.1	5	600min	>50 mg/g	Sharma et al. (2018)
Biochar-CMC-nZVI	Chromium (VI)	5.6	1.25	100	1080min	>99%	Zhang et al. (2019)
CMC-S-nZVI	Chromium (VI)	3.0	Fe dosage=0.3	20	10min	>95%	Zhao et al. (2019)
Two-step CMC-S-nZVI	Trichloroethene	---	Fe dosage=1	10	480min	>80%	Xu et al. (2020)
CMC-AnZVI	Chromium (VI)	3.0	1.5	100	40min	99.9%	Zhao et al. (2022)

4.3. Polyethylene Glycol (PEG)

Polyethylene glycol, a biodegradable and hydrophilic polymer, can enhance the dispersion and stability of zero-valent iron nanoparticles (Zhao et al., 2020). Jiao et al. (2019) synthesized a novel composite of zero-valent iron nanoparticles linked to PEG and stabilized on activated carbon, introducing it as an effective catalyst for hexavalent chromium removal. Zhao et al. (2020) evaluated a sorbent containing zero-valent iron nanoparticles and polyethylene glycol to remove fluoroquinolone antibiotics in water, achieving a high removal efficiency of over 90% within an hour. Wang et al. (2021), in their research on versatile zero-valent iron composites, noted that zero-valent iron nanoparticles modified with PEG efficiently disperse on the substrate surface, showing enhanced performance in reducing pollution due to the presence of numerous hydroxide functional groups. Wang et al. (2022) employed joint modification of zero-valent iron nanoparticles with resin and PEG to remove hexavalent chromium. As depicted in Fig. 4, the resin acts as a carrier and PEG as a stabilizer, preventing agglomeration and oxidation of zero-valent iron nanoparticles. This resulted in a hexavalent chromium adsorption capacity of 134.56 mg/g (Table 3).

Table 3. Different nZVI modified with polyethylene glycol for the pollutant's removal in water

Materials	Contaminant	pH	The catalyst dosage. (g/l)	Initial contaminant Conc.(mg/l)	Time of reaction	Removal efficiency or capacity	Ref.
nZVI–MAC	Chromium (VI)	2.0	4	100	20min	>99%	Jiao et al. (2019)
PZ-NZVI	Norfloxacin	4.0	0.4	10	60min	98.42%	Zhao et al. (2020)
PZ-NZVI	Ofloxacin	4.0	0.5	10	60min	97.62%	Zhao et al. (2020)
1.5PEG-nZVI@BC	Chromium (VI)	3.0	1.25	100	10min	97.38%	Wu et al. (2020)
PEG-nZVI/D201	Chromium (VI)	3.0	3	20	60min	>99%	Wang et al. (2022)

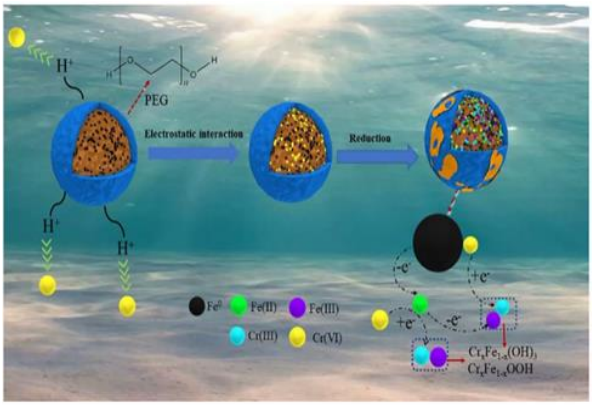

Fig. 4. Removal of Cr (VI) by zero-valent iron nanoparticles stabilized on resin and stabilized by polyethylene glycol (Wang et al., 2022).

4.4. Polyacrylamide (PAM)

Polyacrylamide (PAM) is a synthetic polymer widely used as a flocculent, paper strengthener, and oil recovery enhancer. As a water-soluble polymer, PAM is favored in the biomedical and pharmaceutical sectors, leading to extensive research on its use as a hydrogel for blood-compatible materials. In water and wastewater treatment, PAM is a linker for linking heavy metal ions by forming coordinate bonds (Christy et al., 2020).

Wang et al. (2015) conducted a study in which they observed that introducing Polyacrylamide (PAM) at a concentration of 1 mg/l significantly enhanced the sedimentation of zero-valent iron nanoparticles, thereby improving the wastewater quality. Fig. 5, presented in their study, demonstrated the efficacy of PAM as a support material for zero-valent iron nanoparticles, augmenting their performance in water and wastewater treatment (Table 4).

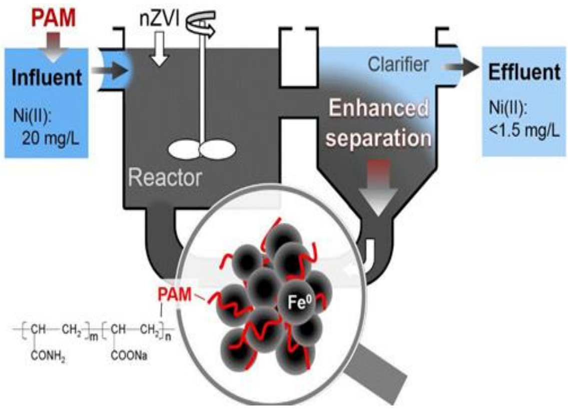

Fig. 5. Reduction of divalent nickel in water using zero-valent iron nanoparticles supported by Polyacrylamide (Wang et al., 2015).

Eljamal et al. (2018) studied the reduction behavior of nitrates and the absorption of phosphorus using zero-valent iron nanoparticles, both in isolation and when stabilized with PAM. Their research demonstrated that among various doses of polyacrylamide, 0.6 grams per liter yielded the highest performance in achieving nitrate removal and phosphorus adsorption.

Moreover, in 2021, the modification of zero-valent iron nanoparticles with polyacrylamide was examined by Liu et al. (2021) Their studies confirmed that compared to bare zero-valent iron nanoparticles, particles modified with PAM become larger and firmer, enhancing the sedimentation rate and water purification (Liu et al., 2021).

Table 4. Various modifications of nZVI with polyacrylamide for the pollutant's removal in water

Materials	Contaminant	pH	The catalyst dosage. (g/l)	Initial contaminant Conc.(mg/l)	Time of reaction	Removal efficiency or capacity	Ref.
PAM enhanced nZVI	Nickel (II)	---	PAM/nZVI = 1:100	100	120 min	92%	Wang et al. (2015)
PAA stabilized nZVI	Nitrate	---	1.25	300	120 min	99%	Eljamal et al. (2018)
PAA stabilized nZVI	Phosphorus	---	1.25	100	120 min	99.2%	Eljamal et al. (2018)
PAA/nZVI	Nitrate	7.0	1	300	120 min	99%	Eljamal et al. (2020)
PAA/nZVI	Phosphorus	7.0	1	100	120 min	97%	Eljamal et al. (2020)

4.5. Polyvinylpyrrolidone (PVP)

Polyvinylpyrrolidone, bearing the chemical formula $(C_6H_9NO)_n$, is known for its water solubility, high dielectric strength, and biodegradability. Due to its unique structural properties, PVP can establish complexes with various mineral salts and perform as a stabilizer, thereby enhancing the physical stability of nanoparticles (Table5) (Tian et al., 2020).

In a study conducted by Chen et al. (2019), a system composed of Polyvinylpyrrolidone and zero-valent iron nanoparticles coupled with copper particles was designed. Implementing of PVP led to an elevated removal efficiency of the antibiotic ciprofloxacin, reaching 95.6% in 120 minutes. Results from BET analyses further affirmed that the inclusion of PVP considerably optimized the specific surface area and dispersion performance of the catalyst.

Similarly, to mitigate the agglomeration issue of zero-valent iron nanoparticles and boost their reactivity, Eljamal et al. (2020) employed four different polymers during the synthesis process. These included polyacrylamide, carboxymethylcellulose, polyethylene sorbitan monolaurate, and Polyvinylpyrrolidone (Fig. 6). The findings indicated that among these, PVP was more effective in enhancing the reactivity of zero-valent iron nanoparticles for nitrate reduction. (The nitrate absorption capacity was observed above 238.9 mg/g).

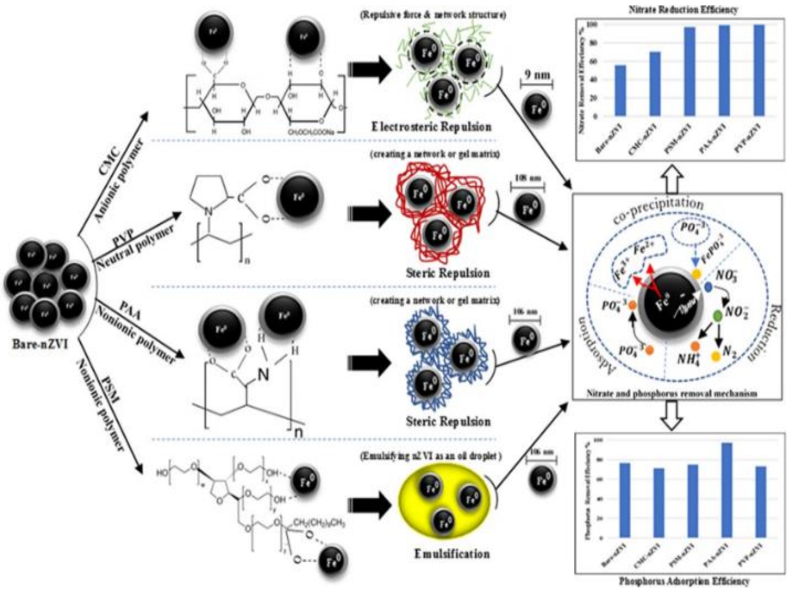

Fig. 6. The impact of different polymers on the support of zero-valent iron nanoparticles for nitrate and phosphorus reduction (Eljamal et al., 2020).

In the Sidorenko et al. (2022) developed a catalyst incorporating zero-valent iron nanoparticles and polyvinylpyrrolidone (PVP) as a stabilizing agent. Analysis of the catalyst's FT-IR spectra revealed bonding facilitated through the oxygen atoms in the PVP's ring structure, which were coordinated with the iron atoms. Furthermore, PVP polymer assisted in generating a negatively charged carbonyl group on the iron nanoparticles' surface during the synthesis, promoting the development of a stable colloidal solution. Large PVP molecules also generated a steric effect, preventing the agglomeration of the particles.

Shamshirgaran et al. (2022) studied the fabrication of zero-valent iron nanoparticles stabilized with Polyvinylpyrrolidone (PVP) and supported by hydrophilic biochar. The hybrid material exhibited an impressive reduction capacity for hexavalent chromium, achieving 99.63% removal in just 5 minutes (Fig. 7). The XPS results indicated that the PVP polymer facilitated the surface absorption process by increasing the number of absorption sites.

The appearance of trivalent chromium on the surface confirmed the conversion of hexavalent chromium, making the impactful role of the polymer in reducing hexavalent chromium evident. Furthermore, BET analysis revealed that although the surface area of the PVP-containing sample decreased slightly compared to the PVP-free sample, there was an increase in the average pore diameter and total pore volume (0.1687 cm^3/g). Investigation of the catalyst's behavior and mechanism also indicated a dominance of absorption in the PVP-free sample and catalytic behavior in the PVP-containing sample.

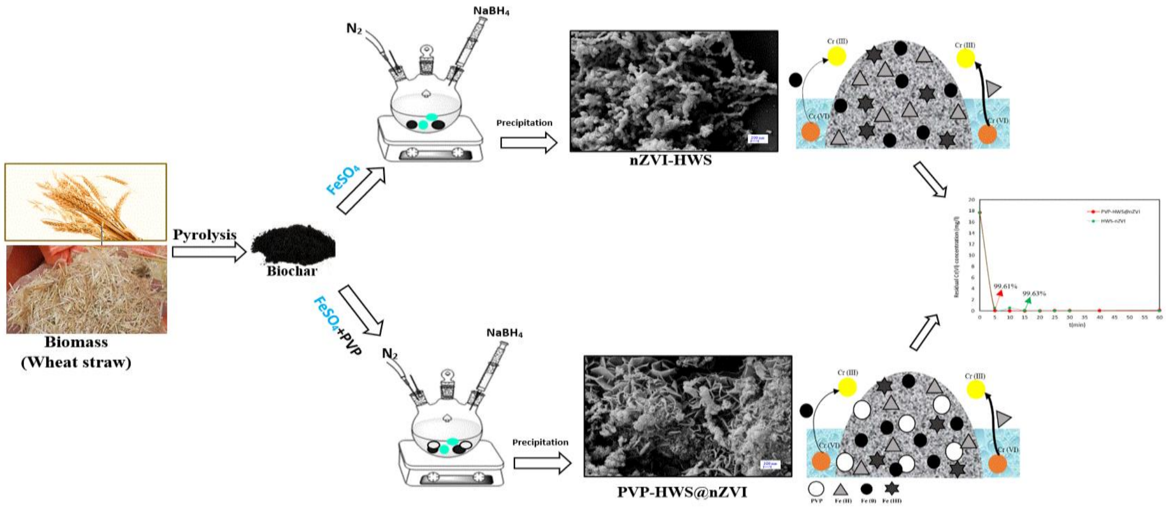

Fig. 7. The effect of PVP polymer on the support of zero-valent iron nanoparticles for Cr (VI) reduction (Shamshirgaran et al., 2022).

Table 5. Some Fe^0 linked to polyvinylpyrrolidone for pollutants removal in water

Materials	Contaminant	pH	The catalyst dosage. (g/l)	Initial contaminant Conc.(mg/l)	Time of reaction	Removal efficiency or capacity	Ref.
PVP-NZVI/Cu	Ciprofloxacin	6.0	1	50	120 min	95.6%	Chen et al. (2019)
PVP/nZVI	Nitrate	7.0	1	300	120 min	99.5%	Eljamal et al. (2020)
PVP/nZVI	Phosphorus	7.0	1	100	120 min	73%	Eljamal et al. (2020)
PVP-nZVI-Cu	Trichloroethylene	3.2	0.4 (by 6 mM of persulfate oxide)	≈1	60 min	99.6%	Idrees et al. (2021)
0.6PVP-nZVI@HWS (2:1)	Chromium (VI)	3.2	0.2	20	5 min	99.63%	Our work

5. Conclusion

Providing clean and sanitary water has always been a paramount concern for humanity. This study examined various methods for reducing organic, mineral, and biological pollutants in water, focusing on the role of nanosorbent, specifically zero-valent iron nanoparticles, in pollutant reduction. Additionally, the study investigated several linkers to enhance the performance of zero-valent iron nanoparticles and mitigate their aggregation. The findings revealed that linkers such as starch, cellulose, polyethylene glycol, polyacrylamide, and Polyvinylpyrrolidone can significantly enhance reaction rates and removal efficiencies. Linkers play a crucial role in supporting nZVI particles and have some advantages, including enhanced stability and compatibility with different media. However, with some disadvantages, such as potential toxicity, limited lifespan, and cost implications. Among these surfactants, Polyvinylpyrrolidone emerged as a hydrophilic, cost-effective, and biodegradable polymer that effectively supports zero-valent iron nanoparticles. The inclusion of Polyvinylpyrrolidone resulted in an increased total pore volume in the composite material. Consequently, Polyvinylpyrrolidone, by augmenting the number of absorption sites, facilitated the surface absorption process, thereby enhancing the efficiency of pollutant reduction.

6. Acknowledgements

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7. Disclosure statement

No potential conflict of interest was reported by the authors.

8. References

Ajith, M. P., Aswathi, M., Priyadarshini, E., & Rajamani, P. (2021). Recent innovations of nanotechnology in water treatment: A comprehensive review. *Bioresource Technology, 342*, 126000-126011.

Al-Amshawee, S., Yunus, M. Y. B. M., Azoddein, A. A. M., Hassell, D. G., Dakhil, I. H., & Hasan, H. A. (2020). Electrodialysis desalination for water and wastewater: A review. *Chemical Engineering Journal, 380,* 122231-122240.

Almasian, A., Giahi, M., Fard, G. C., Dehdast, S. A., & Maleknia, L. (2018). Removal of heavy metal ions by modified PAN/PANI-nylon core-shell nanofibers membrane: Filtration performance, antifouling and regeneration behavior. *Chemical Engineering Journal, 351,* 1166-1178.

Barzegar, G., Jorfi, S., Zarezade, V., Khatebasreh, M., Mehdipour, F., & Ghanbari, F. (2018). 4-Chlorophenol degradation using ultrasound/peroxymonosulfate/nanoscale zero valent iron: reusability, identification of degradation intermediates and potential application for real wastewater. *Chemosphere, 201,* 370-379.

Brasili, E., Bavasso, I., Petruccelli, V., Vilardi, G., Valletta, A., Dal Bosco, C., ... and Di Palma, L. (2020). Remediation of hexavalent chromium contaminated water through zero-valent iron nanoparticles and effects on tomato plant growth performance. *Scientific reports, 10,* 1920-1931.

Chakraborty, R., Asthana, A., Singh, A. K., Jain, B., & Susan, A. B. H. (2022). Adsorption of heavy metal ions by various low-cost adsorbents: a review. *International Journal of Environmental Analytical Chemistry*, *102,* 342-379.

Chen, L., Yuan, T., Ni, R., Yue, Q., & Gao, B. (2019). Multivariate optimization of ciprofloxacin removal by Polyvinylpyrrolidone stabilized NZVI/Cu bimetallic particles. *Chemical Engineering Journal*, *365*, 183-192.

Christy, E. J. S., Rajeswari, A., Gopi, S., & Pius, A. (2020). Chitin and chitosan-based aerogels. Handbook of Chitin and Chitosan.

Connolly, C. T., Cardenas, M. B., Burkart, G. A., Spencer, R. G., & McClelland, J. W. (2020). Groundwater as a major source of dissolved organic matter to Arctic coastal waters. *Nature Communications, 11*, 1479-1487.

Devi, D., Julkapli, N. M., Sagadevan, S., & Johan, M. R. (2023). Eco-friendly green synthesis approach and evaluation of environmental and biological applications of Iron oxide nanoparticles. *Inorganic Chemistry Communications, 152,* 110700-110715.

Eljamal, R., Eljamal, O., & Matsunaga, N. (2018, October). Enhancement of the Reduction and Adsorption Mechanism of nZVI using an effective polyacrylamide as a nonionic polymer, In Proceedings of the Sciences (IEICES) of Fukuoka, Japan Conference.

Eljamal, R., Eljamal, O., Maamoun, I., Yilmaz, G., & Sugihara, Y. (2020). Enhancing the characteristics and reactivity of nZVI: Polymers effect and mechanisms. *Journal of Molecular Liquids*, *315*, 113714-113720.

Elkady, M., Shokry, H., El-Sharkawy, A., El-Subruiti, G., & Hamad, H. (2019). New insights into the activity of green supported nanoscale zero-valent iron composites for enhanced acid blue-25 dye synergistic. decolorization from aqueous medium. *Journal of Molecular Liquids, 294,* 111628-111638.

Elsaid, K., Olabi, A. G., Abdel-Wahab, A., Elkamel, A., Alami, A. H., Inayat, A., ... and Abdelkareem, M. A. (2023). Membrane processes for environmental remediation of nanomaterials: Potentials and challenges. *Science of the Total Environment*, *879*, 162569-162584.

Fida, M., Li, P., Wang, Y., Alam, S. K., & Nsabimana, A. (2022). Water contamination and human health risks in Pakistan: a review. *Exposure and Health*, *14,* 1-21.

Fu, F., Dionysiou, D. D., & Liu, H. (2014). The use of zero-valent iron for groundwater remediation and wastewater treatment: a review. *Journal of hazardous materials, 267,* 194-205.

Habibi, Y. (2014). Key advances in the chemical modification of nanocelluloses. *Chemical Society Reviews*, *43*, 1519-1542.

Hemmat, K., Khodabakhshi, M. R., & Zeraatkar Moghaddam, A. (2021). Synthesis of nanoscale zero-valent iron modified graphene oxide nanosheets and its application for removing tetracycline antibiotic: Response surface methodology. *Applied Organometallic Chemistry, 35*, 6059-6070.

Idrees, A., Shan, A., Ali, M., Abbas, Z., Shahzad, T., Hussain, S., & Lyu, S. (2021). Highly efficient degradation of trichloroethylene in groundwater based on persulfate activation by polyvinylpyrrolidone functionalized Fe/Cu bimetallic nanoparticles. *Journal of Environmental Chemical Engineering*, *9,* 105341-105353.

Jiao, C., Tan, X., Lin, A., & Yang, W. (2019). Preparation of activated carbon supported bead string structure nano zero valent iron in a polyethylene glycol-aqueous solution and its efficient treatment of Cr (VI) wastewater. *Molecules*, *25*, 47-57.

Kordbacheh, F., & Heidari, G. (2023). Water Pollutants and Approaches for their Removal. *Materials Chemistry Horizons, 2,* 139-153.

Kumari, B., & Dutta, S. (2020). Integrating starch encapsulated nanoscale zero-valent iron for better chromium removal performance. *Journal of Water Process Engineering, 37,* 101370-101379.

Lei, C., Sun, Y., Khan, E., Chen, S. S., Tsang, D. C., Graham, N. J., ... and Li, X. D. (2018). Removal of chlorinated organic solvents from hydraulic fracturing wastewater by bare and entrapped nanoscale zero-valent iron. *Chemosphere, 196,* 9-17.

Li, Y. Y., Wang, B., Ma, M. G., & Wang, B. (2018). Review of recent development on preparation, properties, and applications of cellulose-based functional materials. *International Journal of Polymer Science, 218,* 1-18.

Liu, J., Liu, A., Guo, J., Zhou, T., & Zhang, W. X. (2021). Enhanced aggregation and sedimentation of nanoscale zero-valent iron (nZVI) with polyacrylamide modification. *Chemosphere, 263,* 127875-127883.

Liu, Y., Zhang, H., Ding, Y., Hu, N., & Ding, D. (2023). Preparation of carboxy methyl cellulose stabilized nano-sized zero-valent iron and its properties for in situ remediation of groundwater in areas after acid in situ leach uranium mining. *Environmental Science: Water Research and Technology, 9,* 1480-1490.

Lou, Y., Cai, Y., Tong, Y., Hsieh, L., Li, X., Xu, W., ... and Lou, L. (2019). Interaction between pollutants during the removal of polychlorinated biphenyl-heavy metal combined pollution by modified nanoscale zero- valent iron. *Science of the total environment, 673,* 120-127.

Malekzadeh, M., Nejaei, A., Baneshi, M. M., Kokhdan, E. P., & Bardania, H. (2018). The use of starch-modified magnetic Fe0 nanoparticles for naphthalene adsorption from water samples: Adsorption isotherm, kinetic and thermodynamic studies. *Applied Organometallic Chemistry, 32,* 4434-4444.

Mohamed, H. H., Besisa, D. H., Besisa, N., & Youssef, T. E. (2023). Green magnetite nanostructure for removing organic pollutants from water. *Materials Science and Engineering: B, 296,* 116634-116643.

Nasrollahzadeh, M., Sajjadi, M., Iravani, S., & Varma, R. S. (2021). Starch, cellulose, pectin, gum, alginate, chitin and chitosan derived (nano) materials for sustainable water treatment: A review. *Carbohydrate polymers, 251,* 116986-116996.

Ohale, P. E., Igwegbe, C. A., Iwuozor, K. O., Emenike, E. C., Obi, C. C., & Białowiec, A. (2023). A review of the adsorption method for norfloxacin reduction from aqueous media. *MethodsX, 10,* 102180-102201.

Ozaki, H., Ichise, H., Kitaura, E., Yaginuma, Y., Yoda, M., Kuno, K., & Watanabe, I. (2019). Immutable heavy metal pollution before and after change in industrial waste treatment procedure. *Scientific reports, 9,* 1-12.

Pasinszki, T., & Krebsz, M. (2020). Synthesis and application of zero-valent iron nanoparticles in water treatment, environmental remediation, catalysis, and their biological effects. *Nanomaterials, 10,* 917-926.

Peng, H., & Guo, J. (2020). Removal of chromium from wastewater by membrane filtration, chemical precipitation, ion exchange, adsorption electrocoagulation, electrochemical reduction, electrodialysis, electrodeionization, photocatalysis and nanotechnology: a review. *Environmental Chemistry Letters, 18,* 2055-2068.

Qasem, N. A., Mohammed, R. H., & Lawal, D. U. (2021). Removal of heavy metal ions from wastewater: A comprehensive and critical review. *Npj Clean Water, 4,* 1-15.

Romeh, A. A. A. (2023). *Main Green Nanomaterials for Water Remediation*. Green Nano remediation: Sustainable Management of Environmental Pollution

Saleh, T. A., Mustaqeem, M., & Khaled, M. (2022). Water treatment technologies in removing heavy metal ions from wastewater: A review. *Environmental Nanotechnology, Monitoring and Management, 17,* 100617-100627.

Shad, S., Belinga-Desaunay-Nault, M. F. A., Bashir, N., & Lynch, I. (2020). Removal of contaminants from canal water using microwave synthesized zero valent iron nanoparticles. *Environmental Science: Water Research and Technology, 6,* 3057-3065.

Shamshirgaran, R., Malakooti, R., Akbarpour, A., & Moghaddam, A. Z. (2022). Fabrication of Polyvinylpyrrolidone-Stabilized Nano Zero-Valent Iron Supported by Hydrophilic Biochar for Efficient Cr (VI) Removal from Groundwater. *ChemistrySelect, 7,* 1-11.

Sharma, A. K., Devan, R. S., Arora, M., Kumar, R., Ma, Y. R., & Babu, J. N. (2018). Reductive-co-precipitated cellulose immobilized zerovalent iron nanoparticles in ionic liquid/water for Cr (VI) adsorption. *Cellulose, 25,* 5259-5275.

Shrestha, R., Ban, S., Devkota, S., Sharma, S., Joshi, R., Tiwari, A. P., ... and Joshi, M. K. (2021). Technological trends in heavy metals removal from industrial wastewater: A review. *Journal of Environmental Chemical Engineering, 9,* 105688-105706.

Sidorenko, A., Gutul, T., Dvornikov, D., Şeker, M. G., Arit, T., Gutul, E., ... and Vaseashta, A. (2022). Synthesis of nZVI/PVP nanoparticles for bioremediation applications. *Bioremediation Journal, 26,* 162-170.

Siti, N., Mohd, H., Md, L. K., & Shamsul, I. (2013). Adsorption process of heavy metals by low-cost adsorbent: a review. *World Applied Sciences Journal, 28,* 1518-1530.

Stenina, I., Golubenko, D., Nikonenko, V., & Yaroslavtsev, A. (2020). Selectivity of transport processes in ion-exchange membranes: Relationship with the structure and methods for its improvement. *International Journal of Molecular Sciences, 21,* 5517-5526.

Tian, H., Liang, Y., Yang, D., & Sun, Y. (2020). Characteristics of PVP–stabilised NZVI and application to dechlorination of soil–sorbed TCE with ionic surfactant. *Chemosphere, 239,* 124807.

Wang, P., Fu, F., & Liu, T. (2021). A review of the new multifunctional nano zero-valent iron composites for wastewater treatment: Emergence, preparation, optimization and mechanism. *Chemosphere, 285,* 131435-131445.

Wang, S., Zhong, D., Xu, Y., & Zhong, N. (2022). Removal of Hexavalent Chromium from Simulated Wastewater by Polyethylene Glycol–Modified D201 Resin-Supported Nanoscale Zero-Valent Iron. *Water, Air, and Soil Pollution, 233,* 1-15.

Wang, W., Li, S., Lei, H., Pan, B., & Zhang, W. X. (2015). Enhanced separation of nanoscale zero-valent iron (nZVI) using polyacrylamide: performance, characterization and implication. *Chemical Engineering Journal, 260,* 616-622.

Wu, H., Wei, W., Xu, C., Meng, Y., Bai, W., Yang, W., & Lin, A. (2020). Polyethylene glycol-stabilized nano zero-valent iron supported by biochar for highly efficient removal of Cr (VI). *Ecotoxicology and Environmental Safety, 188,* 109902-109912.

Xu, W., Li, Z., Shi, S., Qi, J., Cai, S., Yu, Y., ... and He, F. (2020). Carboxymethyl cellulose stabilized and sulfidated nanoscale zero-valent iron: Characterization and trichloroethene dechlorination. *Applied Catalysis B: Environmental, 262,* 118303-118312.

Yahyaeian, M., Zeraatkar Moghaddam, A., & Fooladi, E. (2023). Use of Efficient and Low-Cost Trimetallic Based on Zero-Valent Iron, Immobilized on Bentonite Surface to Remove Sunset Yellow and Tartrazine Dyes Using Response Surface Optimization Method. *Water, Air, and Soil Pollution, 234,* 79-88.

Yang, C., Ge, C., Li, X., Li, L., Wang, B., Lin, A., & Yang, W. (2021). Does soluble starch improve the removal of Cr (VI) by nZVI loaded on biochar. *Ecotoxicology and Environmental Safety, 208,* 111552-111561.

Yu, Q., Guo, J., Muhammad, Y., Li, Q., Lu, Z., Yun, J., & Liang, Y. (2020). Mechanisms of enhanced hexavalent chromium removal from groundwater by sodium carboxymethyl cellulose stabilized zerovalent iron nanoparticles. *Journal of Environmental Management, 276,* 111245-111254.

Zafar, A. M., Javed, M. A., Hassan, A. A., & Mohamed, M. M. (2021). Groundwater remediation using zero-valent iron nanoparticles (nZVI). *Groundwater for Sustainable Development, 15,* 100694-100704.

Zhang, S., Lyu, H., Tang, J., Song, B., Zhen, M., & Liu, X. (2019). A novel biochar supported CMC stabilized nano zero-valent iron composite for hexavalent chromium removal from water. *Chemosphere, 217,* 686-694.

Zhao, J., Yang, X., Liang, G., Wang, Z., Li, S., Wang, Z., & Xie, X. (2020). Effective removal of two fluoroquinolone antibiotics by PEG-4000 stabilized nanoscale zero-valent iron supported onto zeolite (PZ-NZVI). *Science of the Total Environment, 710,* 136289-136299.

Zhao, K., Yang, L., Qian, L., Zhang, Y., Hou, J., Christie, P., ... and Qi, P. (2022). Elimination of Chromium (VI) and Vanadium (V) from Waters by Carboxymethylcellulose-Stabilized Amorphous Nanoscale Zero-Valent Iron. *Water, Air, and Soil Pollution, 233,* 1-14.

Zhao, L., Zhao, Y., Yang, B., & Teng, H. (2019). Application of carboxymethyl cellulose–stabilized sulfidated nano zerovalent iron for removal of Cr (VI) in simulated groundwater. *Water, Air, and Soil Pollution, 230,* 1-14.

Zhu, K., Gao, Y., Tan, X., & Chen, C. (2016). Polyaniline-modified Mg/Al layered double hydroxide composites and their application in efficient removal of Cr (VI). *ACS Sustainable Chemistry and Engineering, 4,* 4361-4369.

Zhu, S., Ho, S. H., Huang, X., Wang, D., Yang, F., Wang, L., ... and Ma, F. (2017). Magnetic nanoscale zerovalent iron assisted biochar: interfacial chemical behaviors and heavy metals remediation performance. *ACS Sustainable Chemistry and Engineering, 5,* 9673-9682.