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# Insights into micro-and nano-zero valent iron materials: synthesis methods and multifaceted applications

 Murtala Namakka,<sup>\*ab</sup> Md Rezaur Rahman,  <sup>\*a</sup> Khairul Anwar Bin Mohamad Said<sup>a</sup> and Adamu Muhammad<sup>c</sup>

The growing threat of environmental pollution to global environmental health necessitates a focus on the search for sustainable wastewater remediation materials coupled with innovative remediation strategies. Nano and micro zero-valent iron materials have attracted substantial researchers' attention due to their distinct physicochemical properties. This review article delves into novel micro- and nano-zero valent iron (ZVI) materials, analysing their synthesis methods, and exploring their multifaceted potential as a powerful tool for environmental remediation. This analysis contributes to the ongoing search of effective solutions for environmental remediation. Synthesis techniques are analysed based on their efficacy, scalability, and environmental impact, providing insights into existing methodologies, current challenges, and future directions for optimisation. Factors influencing ZVI materials' physicochemical properties and multifunctional engineering applications, including their role in wastewater and soil remediation, are highlighted. Environmental concerns, pros and cons, and the potential industrial applications of these materials are also discussed, accenting the importance of understanding the synthesis methods, materials' applications and their impacts on humans and the environment. The review is designed to provide insights into nano-and micro-ZVI materials, and their potential engineering applications, as well as guide researchers in the choice of ZVI materials' synthesis methods from a variety of nanoparticle synthesis strategies fostering nexus between these methods and industrial applications.

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## 1 Introduction

In the past two decades, significant progress has been made in developing efficient materials and synthesis strategies for environmental remediations to address soil and wastewater pollution.<sup>1-3</sup> Nano and micro zero-valent iron (ZVI) materials have emerged as effective materials due to their exceptional capacity to degrade a wide range of environmental contaminants.<sup>4-8</sup> These novel materials are derived from their precursor iron materials through a plethora of synthesis strategies.<sup>9-12</sup> Iron is a naturally occurring material that ranks as the fourth most abundant element after oxygen, silicon, aluminium, and constitutes about 5% of Earth's crust by mass.<sup>13-15</sup> Iron is naturally found in the form of ore, a naturally occurring mineral aggregate combined with gangues. Iron ores enveloped vital minerals, such as magnetite Fe<sub>3</sub>O<sub>4</sub>,<sup>13,16-20</sup> Haematite Fe<sub>2</sub>O<sub>4</sub>,<sup>21-23</sup> Goethite Fe<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O,<sup>19,24</sup> Pyrrhotite Fe(1-x)S<sup>17,19,25</sup> Limonite 2Fe<sub>2</sub>O<sub>3</sub>·3H<sub>2</sub>O,<sup>26,27</sup> Siderite FeCO<sub>3</sub>,<sup>28,29</sup>

Pyrite FeS<sub>2</sub>,<sup>30,31</sup> and Ilmenite FeTiO<sub>3</sub> (ref. 32 and 33) with their iron contents decreasing order from magnetite to Ilmenite.<sup>34</sup> Iron minerals have a wide range of engineering applications and utilized in several industries.<sup>35,36</sup> Iron occurs in either 0, +2, or +3 oxidation states which are more occurrent than +4, +5 and +6 oxidations. However, significant tendencies of reduced oxidation (see eqn (1)) exist even at standard conditions which is most common in the case of aqueous Fe<sup>3+</sup> to Fe<sup>2+</sup>.



Iron oxides particularly magnetite and haematites usually release metallic irons when heated in the presence of a reducing agent.<sup>13,18,37</sup> However, the reconditens of this approach lies on the purity of the metal compounds produced as well as their physical and chemical properties since various applications require distinct chemical and morphological characteristics of iron compounds. In addition to chemical reaction, magnetism significantly influences the role of iron compounds in many engineering applications like catalysis, biomedicine, and magnetic fluids. As a result, several synthesis strategies of producing iron materials are explored. Apart from conventional utilization of iron materials in agriculture, metal, mechanic, and steel industries, recent technological advancement has

<sup>a</sup>Department of Chemical Engineering and Energy Sustainability, Faculty of Engineering, University Malaysia Sarawak, 94300, Kota Samarahan, Malaysia. E-mail: 22010290@siswa.unimas.my; rmrezaur@unimas.my

<sup>b</sup>Ahmadu Bello University Zaria, Kaduna state, Nigeria

<sup>c</sup>Nigerian National Petroleum Corporation Limited, NNPC, Nigeria



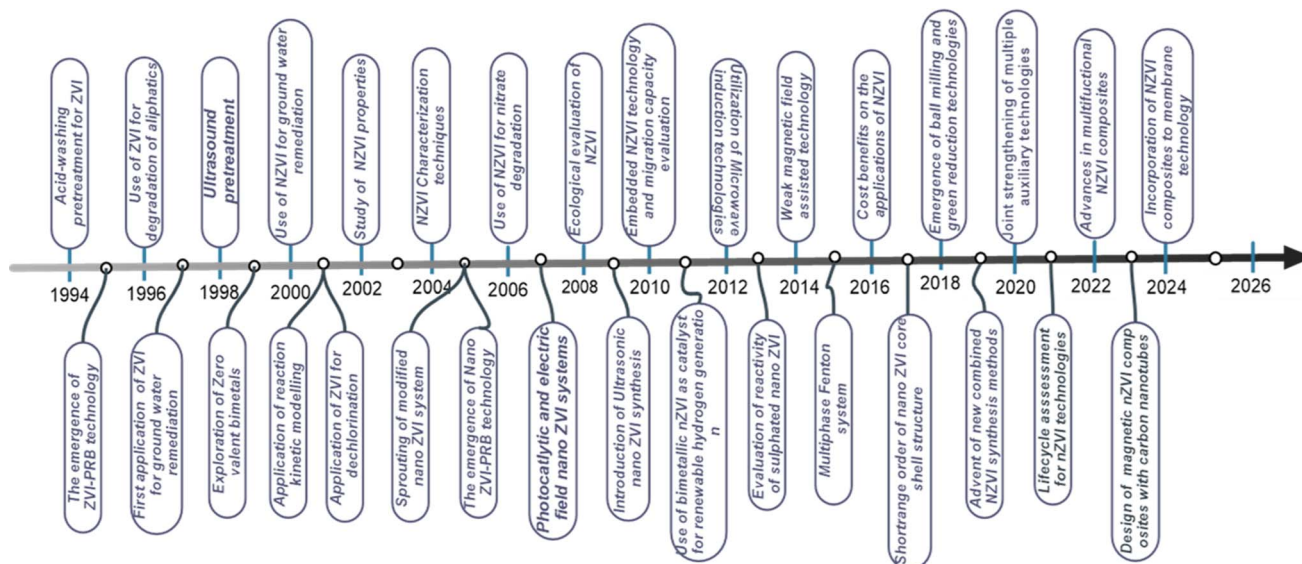


Fig. 1 History and research advances on nano and micro ZVI and their composites.

seen the use of iron precursors in the extraction of crucial metal compounds which are used as catalysts for environmental remediation<sup>14,15,38</sup> among a plethora of other applications.<sup>23</sup> These advancements include the fabrication of micro and nano zerovalent iron materials (nano and micro-ZVI).<sup>39</sup> Micro-ZVI (micro-zero valent iron) materials were discovered to be significantly effective in groundwater remediations since 1997.<sup>40</sup> And have ever since attracted researchers' attention owing to their cost effectiveness, non-toxicity,<sup>41,42</sup> and potentials for industrial effluents and wastewater remediation.<sup>43,44</sup> Fig. 1 provides research advances on nano and micro-ZVI and their composites.

Despite the potentials of micro-ZVI materials, rapid passivation and demand for special material properties necessitated their encapsulation with supportive materials,<sup>45–48</sup> forming stabilized nanocomposites with enhanced reactivity and reduced passivation.<sup>49–53</sup> However, chemical reactivity and photocatalytic activity were yet hindered by limited active sites in addition to particle agglomeration.<sup>54,55</sup> Unlocking the full potential of these materials, producing nanoparticles with multiple active sites coupled with enhanced physicochemical properties *viz.* strong reducing power, and diverse functionalities to suite demanding engineering applications, hinges on a comprehensive understanding of their physicochemical properties, evolving synthesis strategies, and application fields. Although previous reviews have addressed individual aspects,<sup>56,57</sup> a critical and consolidated analysis of both synthesis strategies and application landscapes remains elusive. This review bridges this gap in the literature by providing a concise insight into nano and micro-ZVI materials, synthesis methods, and their extensive and developing range of applications, including their functions in groundwater, industrial wastewater, soil, sludge, and waste treatment. The review explores the basic concepts of these synthesis methods, their environmental impacts, influence synthesis methods on

properties and surface characteristics of the synthesized materials, and the existing and prospective engineering applications of nano and micro-ZVI materials. The article is organised into four sections. The first section provides basic background on ZVI materials and their iron precursors, followed by brief overview of nano and micro-ZVI materials, factors influencing nano and micro-ZVI materials properties and performance, a general overview of nanoparticle synthesis methods. Section two provides comprehensive overview of nano and micro-ZVI materials synthesis strategies and comparison of physicochemical properties and performance of materials synthesized. Section three discusses existing and prospective applications with environmental considerations. Section four finalized with conclusions and future perspectives.

## 2 Nano and micro zerovalent irons (nano and micro-ZVI)

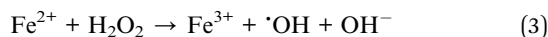
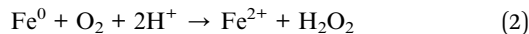
### 2.1 Micro zero valent iron (micro-ZVI)

Micro zero-valent iron (mZVI) is a fine, black powder derived from iron that exhibits a zero oxidation state, it is characterized by high surface area,<sup>58</sup> chemical reactivity,<sup>59,60</sup> and employed in various environmental and engineering applications, particularly in the field of contaminant remediation.<sup>61</sup> ZVI materials are favourable option for environmental remediation owing to their unique combination of desirable properties, *viz.* They are considerably non-toxic, readily available, inexpensive, and easily produced while requiring minimal maintenance for their chemical reductive processes.<sup>62</sup> Their reactivity stem from their standard redox potential ( $E_0 = -0.44$  V), rendering them effective reductants for oxidizing contaminants like Cr(VI).<sup>63,64</sup> The primary reaction mechanism of mZVI materials involve direct electron transfer from mZVI to the contaminant.<sup>65</sup> Extensive researches established the efficacy of advanced oxidation processes (AOPs) of ZVI in wastewater treatment.<sup>66</sup> In these

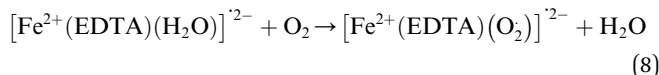
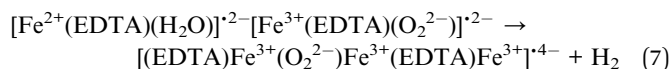
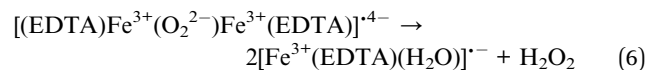
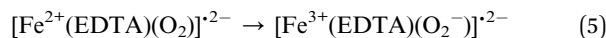
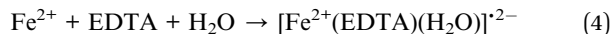


## Review

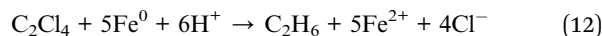
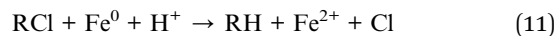
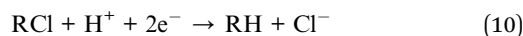
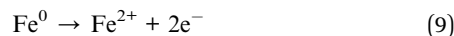
processes, ZVI materials degrade organic contaminants into smaller, less harmful molecules.<sup>43</sup> Additionally, zero valent iron Fe<sup>0</sup>-based Fenton-like reactions generate reactive oxygen species (ROSS) capable of decomposing organic pollutants present in wastewater.<sup>67</sup> Moreso, under acidic conditions, in the presence of dissolved oxygen (O<sub>2</sub>), zero-valent iron (Fe<sup>0</sup>) produces hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), a key precursor for ROS generation in Fenton-like systems.<sup>68</sup> These reaction mechanisms, from eqn (1), are outlined below.



As shown in eqn (1) to (3), the hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) which subsequently reacted with iron(II), was formed through electron transfer from ZVI in the presence of oxygen. ZVI exhibits the ability to degrade and oxidize various organic compounds in the presence of dissolved oxygen (DO) as shown in the reactions above. This process involves ZVI transferring two electrons to O<sub>2</sub>, resulting in the formation of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). Subsequently, H<sub>2</sub>O<sub>2</sub> undergoes chemical reduction to produce water *via* another two-electron transfer from ZVI. Interestingly, the Fenton reaction, involving the combination of H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup> generates hydroxyl radicals ( $\cdot\text{OH}$ ) with potent oxidizing capabilities against diverse organic compounds, which are otherwise generated through either photo-Fenton of iron(ii or iii) or UV irradiation.<sup>69</sup> In addition to Fenton reaction mechanism, ZVI core-shell model<sup>70</sup> emerged for contaminant removal. Vast evidences support the presence of a core-shell structure in ZVI and several chemical reactions occurring on its surface.<sup>70-72</sup> While the metallic iron core serves as the electron donor, facilitating pollutant reduction,<sup>70,73,74</sup> the surrounding iron oxide shell acts as an adsorption platform for contaminant accumulation.<sup>73</sup> This conceptual model has proven adept at explaining phenomena such as adsorption, reduction, oxidation, and precipitation that occur near the ZVI surface. However, the core-shell framework currently falls short of providing the quantitative insights necessary for designing and optimizing ZVI-based wastewater treatment processes.<sup>75</sup> To achieve this, dynamic reaction kinetic models capturing the complex phenomena around ZVI particles are a requisite, particularly for quantifying the impacts of operating parameters on heavy metal removal efficiency. Coincidentally, the suitability of modified Fenton like reaction was assessed.<sup>76</sup> Zhou *et al.* (2018) incorporated magnetic field and ZVI/ethylenediaminetetraacetic acid (EDTA) Fenton like system to quantify ZVI degradation of nonsteroidal anti-inflammatory diseases (NSAIDs). The magnetic field primarily influences surface-bound reactions on heterogeneous ZVI material surface thereby accelerating its corrosion. Interestingly, this influence remains restricted to surface phenomena, with no impact observed on the homogeneous iron cycle or Fenton-like reactions within the bulk ZVI material.<sup>76</sup> However, the oxidation potential depends on the type and structural properties of ZVI materials. The modified reactions are as follows.



Zero-valent iron (ZVI) materials possess remarkable flexibility in their ability to transform a diverse range of environmental contaminants through direct contact.<sup>34,77</sup> Among these contaminants include halogenated hydrocarbons such as chlorinated methane. The direct contact reaction mechanism of ZVI in the degradation of chlorinated methane was reported in ref. 78, the mechanism is briefly described here as follows.



From the above reactions, R represent an alkyl group such as methane, ethane *etc.* ZVI (zero valent iron) initiates the reaction by donating electrons to the chlorinated hydrocarbon (RCl), which subsequently underwent de-chlorination leading to the formation of RH + Cl<sup>-</sup>. Introducing ZVI to this step produces an oxidized iron with a chlorine byproduct indicating ZVI requirements and its favourable conditions in completely degrading chlorinated hydrocarbons like tetrachloromethane (C<sub>2</sub>Cl<sub>4</sub>).<sup>79</sup> Several factors including operating conditions and intrinsic metal characteristics influence the performance of ZVI materials in the removal of environmental contaminants.<sup>65</sup> Operating conditions such as temperature, iron concentrations and pH are more pronounced (see Fig. 2 and 3). Shimizu *et al.*,<sup>81</sup> revealed the mechanism of phenol removal by zero-valent iron (ZVI) in the presence of dissolved oxygen by varying the pH from 2 to 8.1, pH and dissolved oxygen was found to significantly influence iron dissolution while OH radical production was an important parameter. At pH 3, 91% phenol removal was achieved with a 24% reduction in total organic carbon (TOC), of which 77% was attributed to the Fenton reaction, while at pH 4 and 5, adsorption/precipitation dominated DOC removal, and minimal TOC reduction was observed at pH 2 and 8.1.<sup>81</sup> Other research findings show that 3.0 is the optimal pH for NB degradation within the tested pH range of 3.0 to 12.0. While the rate of formation of aniline, a major reductive product of NB, follows zero-order kinetics at various pH levels.<sup>82,83</sup>

Similarly, Wang *et al.*, observed the efficiency in the treatment of lead contaminated soils by zero valent iron materials to



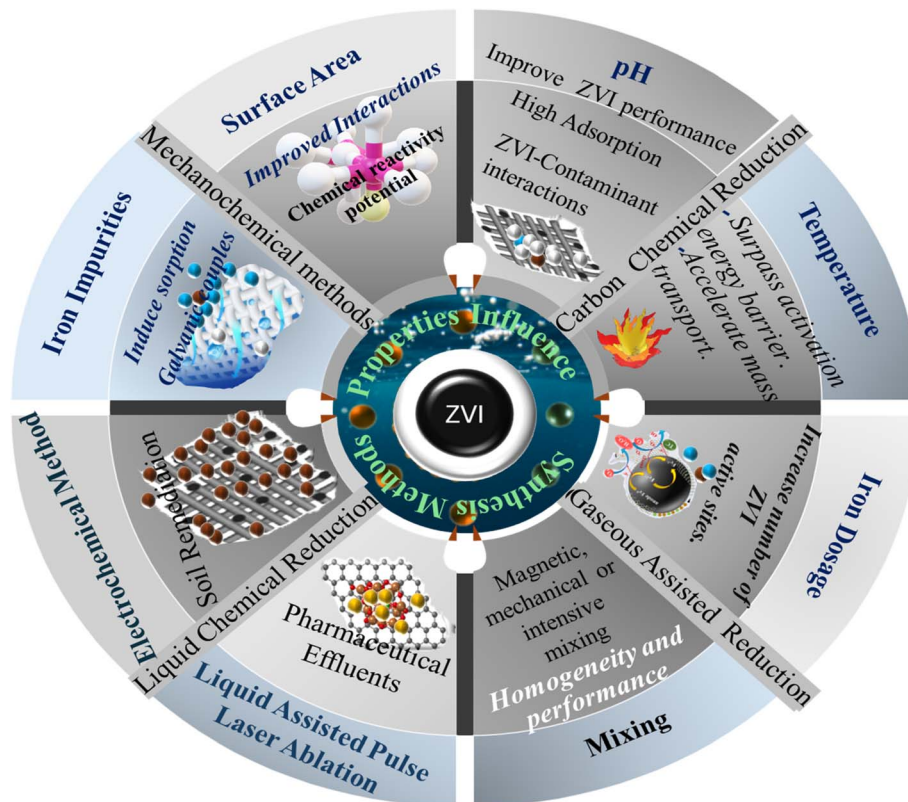


Fig. 2 Strategies and influence of process conditions and iron characteristics on the performance of micro-ZVI materials.

decrease with increasing pH from 3 to 9.<sup>84</sup> Fig. 3 shows how varying concentration of nano and micro-ZVI influenced their performance. Micro ZVI materials can be used to transform organic dyes and pesticides: including dichlorodiphenyltrichloroethane, (DDT),<sup>85</sup> lindane, and other dye molecules,<sup>86–89</sup> inorganic anions like dichromate, perchlorate, nitrate, and arsenic. ZVI material performance in the degradation of persistent organic pollutants such as polychlorinated biphenyls, dioxins, pentachlorophenol, *N*-nitrosodimethylamine and TNT were also reported.<sup>34,78</sup> However, ZVI materials are limited by low sorption affinity in degrading organic contaminants, which is a typical characteristic of pristine iron oxides.<sup>85</sup> Hence, supportive adsorbent such as graphene or activated carbon<sup>90</sup> are often incorporated to ZVI materials when applied in an emerging organic pollutants medium.

ZVI (Zero Valent Iron) materials' applications span across many fields, profoundly in groundwater and soil remediations like the removal of organophosphates,<sup>91</sup> heavy metals,<sup>92</sup> dyes, anti-biotics,<sup>93</sup> and other organic contaminants.<sup>85,94–97</sup> Emerging contaminants such as polyhalogenated carbazoles (PHCZs) are persistent, bio-accumulative, and toxic environmental contaminants lacking efficient and sustainable degradation method, coupling micro-ZVI with supportive adsorbents has indicated a promising activity in degrading these types of contaminants.<sup>75,82,98–100</sup> Such as the use of sulfidated zero-valent iron combined with peroxydisulfate (S-ZVI/PMS).<sup>101</sup> Similar research by Wang *et al.*, (2023)<sup>102</sup> and<sup>103,104</sup> with 96.6% Cr(vi) removal, thiobencarb removal,<sup>105</sup> degradation of

oxytetracycline<sup>106,107</sup> and degradation of clopyralid and MTBE, tetrachloroethene.<sup>95</sup> By and large, it is imperative to note that both micro and nano ZVI material's characteristics depend on the intrinsic properties and mineralogical compositions of the precursors. Consequently, the core-shell model, Fenton reaction mechanism and modified Fenton like mechanisms have found common use in revealing the efficacy and mechanism of ZVI interactions with contaminants owing to their understood technology plus the availability of research findings on these mechanisms since the introduction of PRB technologies in the early 1990s (refer to Fig. 1). Distinct material properties requirements such as increased chemical reactivity, higher surface area to volume ratio for an increased number of active sites coupled with low agglomeration demands led to the emergence of nano zero-valent iron materials or simply nZVI as a research area.

## 2.2 Nano zero valent iron (nano-ZVI)

Nano ZVI (Zero Valent Iron) is a fine, black powder derived from micro-ZVI through chemical and physical synthesis methods and characterized by smaller particle sizes within the nano scale (between 1 nm to 100 nm) range.<sup>72,108</sup> nZVI is distinguished by its excellent surface area with higher chemical reactivity, and numerous active sites (see Fig. 4). It provides sufficient surface area and excellent interaction with emerging contaminants.<sup>109,110</sup> The high surface area and reactivity of nZVI materials translate to improved effects and superior performance compared to their microscale counterpart.<sup>34,111</sup>



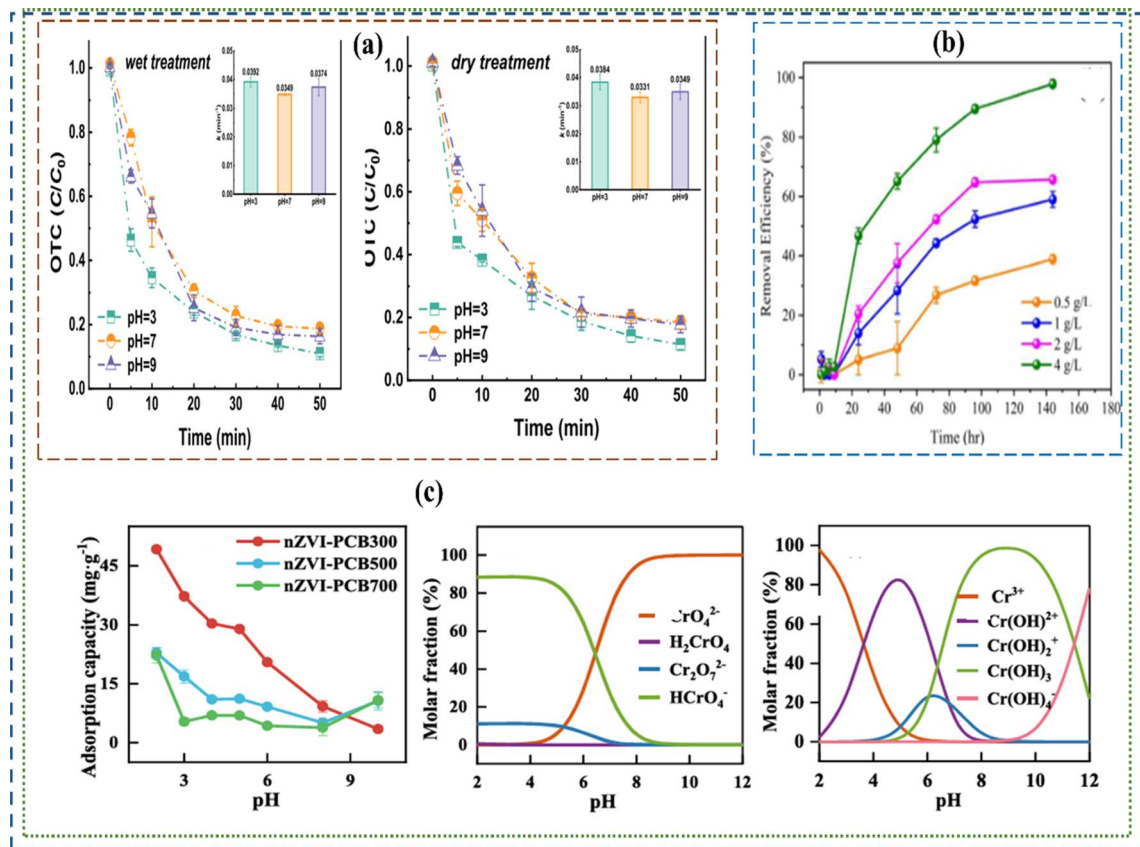


Fig. 3 Influence of concentrations and pH on the performance of nano and micro-ZVI materials in the removal and adsorption of contaminants. (a–c) show the impacts of pH variation on removal chromium, and the influence of concentration of nano and micro-ZVI composites on oxytetracycline and chromium degradation<sup>80</sup> Copyright: 2024, Elsevier.

The unique attributes of nano-ZVI materials that distinguish them from micro-ZVI stems predominantly from their increased surface-to-volume ratio and/or the enhanced reactivity of their surface sites.<sup>6</sup> As ZVI (Zero Valent Iron) particle size diminishes, the proportionate contribution of surface atoms increases, significantly amplifying their propensity to adsorb, interact, and react with other atoms, molecules, and complexes (refer to Fig. 4). This amplified reactivity can be ascribed to the greater access and availability of active sites on

the nZVI particle surface, aiding charge stabilization through electronic interactions with surrounding atoms.<sup>112</sup> Recent researches highlight the remarkable potentials of nano ZVI for degrading diverse inorganic contaminants,<sup>110</sup> including metal ions,<sup>113</sup> like Cd,<sup>114</sup> Cr,<sup>115–118</sup> complex anions like perchlorate and nitrate.<sup>82,119–122</sup> Compared to conventional sorbents and their interactions with other iron particles, nZVI materials offer significant advantages and exhibit substantially higher capacity for contaminant removal as also exemplified by their ability to

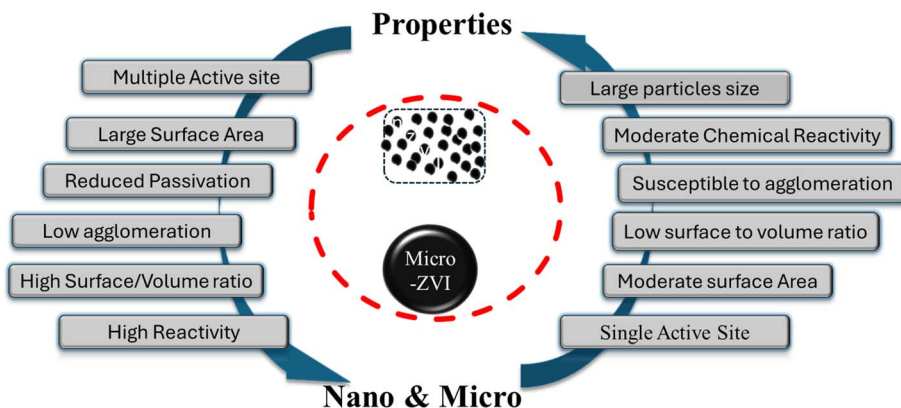


Fig. 4 Comparison of reaction active sites and properties of micro and nano ZVI materials.



remove mixed dyes<sup>86,123,124</sup> and heavy metals like Cr(vi)<sup>125</sup> and Ni(II) efficiently from wastewater through reduction and co-precipitation usually at both lower and higher pH<sup>126</sup>. Moreover, nZVI possesses faster reaction rates, with studies showing at least 25–30 times higher efficiency in Cr(vi) removal compared to microscale ZVI.<sup>127</sup> In addition, n-ZVI when stabilized with other materials such as carboxymethyl cellulose, CMC, and nZVI materials significantly enhances dye degradation from textile wastewater.<sup>128</sup>

Nanosized zero-valent iron (nZVI) materials offer enhanced environmental remediation capabilities due to their increased specific surface area, leading to a greater abundance of active reaction sites (refer to Fig. 4) compared to their corresponding micro-scaled counterpart. However, a key challenge arises owing to the inherent magnetic properties of nZVI, which often cause particle aggregation.<sup>75</sup> These formed aggregates possess paradoxical properties and enhance magnetic mobility for targeted delivery with a reduced surface area, causing nZVI material's reactivity. To address this and optimize both reactivity and mobility, extensive research efforts have focused on tailoring the synthesis methods of nZVI particles.

### 2.3 Overview of nanoparticle synthesis methods

Nanoparticle synthesis methods are classified into either top-down and bottom-up approaches or simply physical and chemical synthesis methods.<sup>108</sup> Fig. 5 gives an overview these classifications.

Physical/top-down methods are effective in fabricating nanomaterials with distinct properties and applications.<sup>108</sup> However, in addition to being energy intensive, the properties of the developed nanoparticles are often altered, limiting their applications in material synthesis that require stringent control over morphological structures.<sup>108</sup> Bottom-up/chemical synthesis methods involve the use of chemical reactions to manipulate atoms or molecules to form nanoparticles. In contrast, chemical methods allow a degree of control over the morphological structure of the synthesized nanomaterials.<sup>108</sup> Green synthesis methods are recently discovered viable,<sup>108,129–131</sup> paving the way for utilizing biobased materials as a sustainable source of nanoparticles for various applications.<sup>108</sup>

### 2.4 Synthesis methods of zerovalent iron micro and nano materials

There are several synthesis methods of nano and micro zerovalent iron materials ranging from bottom-up approaches to green synthesis and combined technologies each with its distinguishing applications, materials properties, and limitations.<sup>132–138</sup>

**2.4.1 Mechanical ball milling.** Ball milling refers to the breaking down of iron precursor material into micro or nano-scale particles through a high-speed rotating chamber.<sup>108,139,140</sup> The ball-milling approach is regarded as one of the most sustainable for synthesizing nanocomposites and wear spray coatings.<sup>141–143</sup> Imperative factors in this approach are the container size, and the energy input.<sup>108,144,190</sup> Ball milled

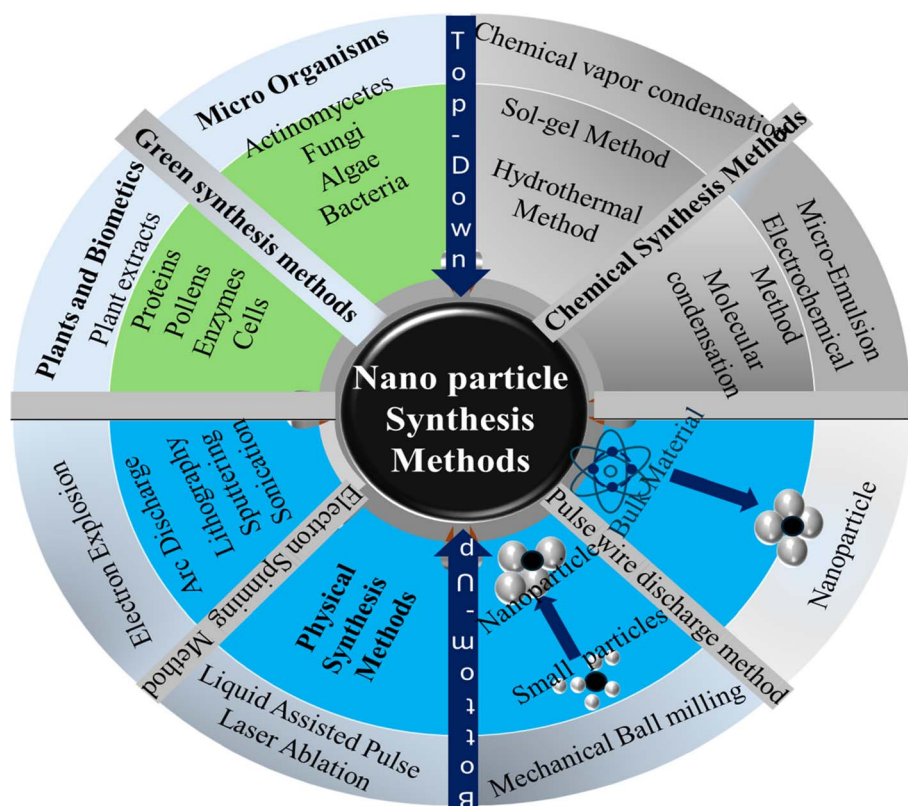


Fig. 5 Overview of nanoparticles synthesis methods: top-down and bottom-up approaches.



nanoparticles are highly efficient in the degradation of wastewater contaminants,<sup>77,145</sup> and their composites recorded high efficacy in soil remediations.<sup>125,146</sup>

**2.4.2 Mechanochemical method.** Mechanochemical synthesis is a combined synthesis method that involves the use of mechanical energy such as friction or shear force for the initiation of chemical reactions.<sup>133</sup> It's usually combined with ball milling to provide sufficient mechanical energy for the bulk or micro-scale iron particles to disintegrate into nano-scaled particles<sup>133,147</sup> and provides sufficient access to active sites of nanocomposites materials.<sup>132</sup> Mechanochemical method produces ZVI materials with an increased particle reactivity potential compared to conventional mechanical ball milling procedure.<sup>134</sup>

**2.4.3 Chemical vapor deposition method.** Chemical vapor deposition can be physical or chemical process depending on the nature and compositions of the reacting materials.<sup>148</sup> The procedure involves vaporizing target materials and condensing them with chemical methods altering the target material's composition to form nanocomposite materials.<sup>149,150</sup> The produced nanoparticles condense into liquid nitrogen before subsequent morphological changes.<sup>148</sup> In addition to control over material properties, chemical vapor deposition produces nano materials with significantly lower agglomeration potential.

**2.4.4 Liquid -assisted pulsed laser ablation.** Liquid-assisted pulsed laser ablation (LA-PLA) synthesis method refers to the formation of nanoparticles with varying sizes, crystallinity, and shell composition using femtosecond pulse laser in water, or a nanosecond pulse laser on bulk iron targets immersed in different organic solvents. The properties of the synthesized materials are proportional to the nature of the solvent used and the pulse overlap.<sup>151</sup> Pulse laser is cost effective, and environmentally benign.<sup>151,152</sup>

**2.4.5 Liquid assisted chemical reduction.** The liquid chemical reduction approach is the most utilized method of synthesizing micro-nano ZVIs (Zero Valent Iron),<sup>153</sup> by chemically reacting suitable iron precursor with sodium borohydride ( $\text{NaBH}_4$ ) or any other suitable reducing agent,<sup>154</sup> the reaction is conducted under nitrogen condition.<sup>155</sup> Black colour particles emerge immediately after the addition of sufficient solution of the reducing agent.,<sup>156</sup> Fig. 6 shows the synthesis route in the liquid-assisted chemical reduction of selected nano and micro-ZVI materials.

**2.4.6 Gaseous chemical reduction.** In the gaseous chemical reduction method, hydrogen is the primary reducing agent.<sup>160</sup> Iron precursors such as goethite,<sup>161</sup> magnetite<sup>162</sup> or limonite<sup>27</sup> are first produced through precipitation of ferrous salts and then dehydrated or heated to prepare them for chemical reduction. The method starts by reducing the iron precursors

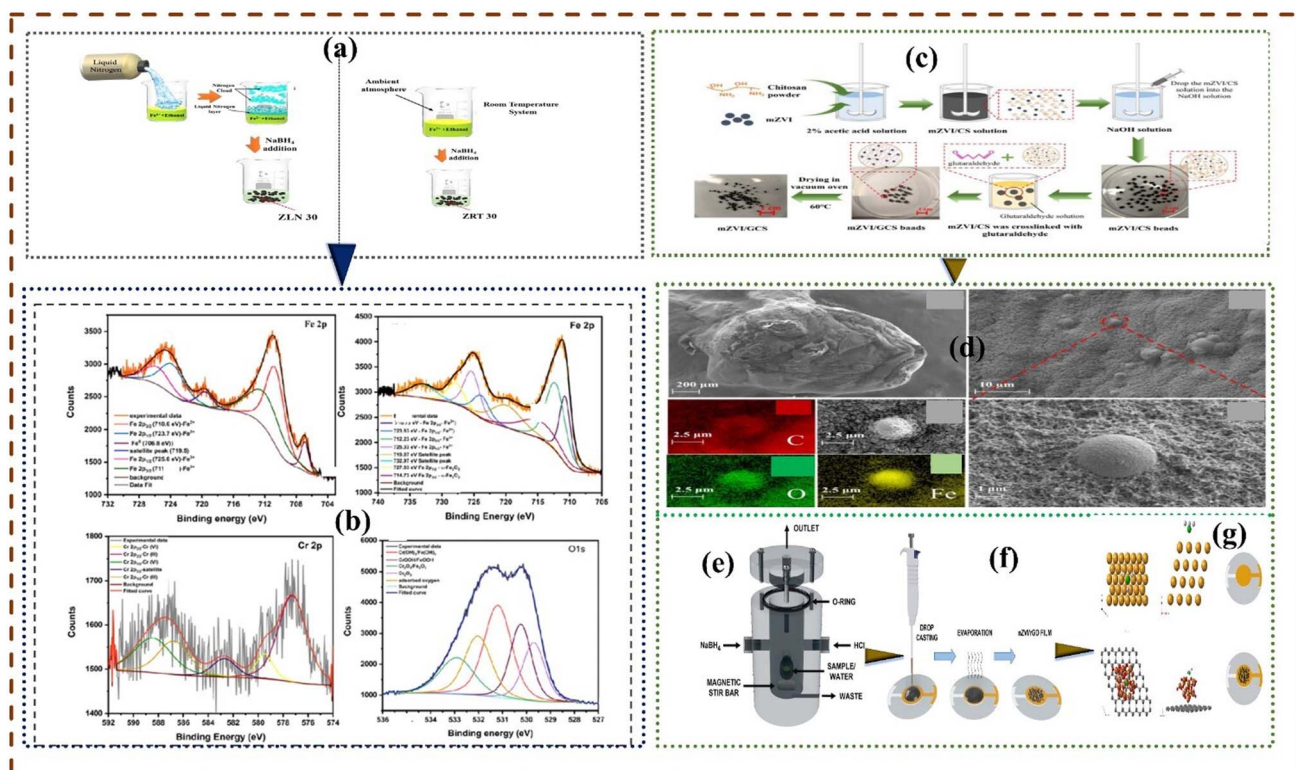


Fig. 6 Sodium borohydride ( $\text{NaBH}_4$ ) assisted chemical reduction methods. Methodology for synthesizing liquid nitrogen-assisted zerovalent iron (ZLN) (a and b), energy peaks and chemical composition of ZLN observed from iron 2p before and after reactions (b)<sup>157</sup> Copyright: 2023, Elsevier. Synthesis pathway of micro-ZVI coupled glutaraldehyde crosslinked chitosan (c) micro-ZVI morphological structures (d).<sup>158</sup> Synthesis route of nano ZVI coated reduced graphene oxide (nZVI/rGO) (e and f), lateral, top, and unmodified adsorption of arsine  $\text{AsH}_3$  by nZVI/rGO (g)<sup>159</sup> Copyright: 2024, Elsevier.



(obtained through precipitation), at elevated temperatures with hydrogen gas,<sup>37</sup> followed by chemical reduction in a hydrogen or nitrogen gas-controlled environment.<sup>160</sup> The gaseous chemical reduction synthesis method yields nano and micro-ZVI materials with controlled surface properties.<sup>150</sup>

**2.4.7 Carbo-thermal reduction.** The carbo-thermal synthesis method is a high-temperature reduction of iron precursors using thermal energy in the presence of gaseous reducing agents.<sup>163–165</sup> The resulting coupled ZVI-carbon products are obtained through chemical reactions with carbon materials.<sup>166,167</sup> The synthesized nZVI-supported carbon particles exhibit enhanced physicochemical properties,<sup>168</sup> low agglomeration characteristics,<sup>169–171</sup> and high degradation activity in relation to non-carbon encapsulated ZVI materials.<sup>172</sup> Carbothermal synthesis method is highly suitable for producing carbon encapsulated iron materials with chemical byproducts compared to conventional chemical reduction methods.<sup>173</sup>

**2.4.8 One spot chemical method.** One spot synthesis method is a combined technology usually accompanied by liquid chemical reduction where iron precursors such as  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  are dissolved and mixed with reacting/supporting material under nitrogen gas,  $\text{N}_2$  atmosphere.<sup>154,174</sup> It is cost-effective and produces iron materials with significant stability and low aggregation. Fig. 7 shows one spot chemical synthesis routes for producing nano zero-valent iron composite materials.

**2.4.9 Electrochemical reduction.** The electrochemical method uses an electrolysis process to produce nano and micro-ZVI materials.<sup>175–177</sup> This method involves introducing iron precursors like iron pentacarbonyl, argon gas, ethylene, acetylene, and ethyl materials into a reaction chamber while gas current is rapidly expanded in two phases to control nanoparticle growth and agglomeration.<sup>178</sup> The ZVI (Zero Valent Iron) materials nanoparticles condense into a liquid nitrogen substrate and transferred to a delivery system for collection after undergoing structural changes through purification, and crystallization.<sup>150,175</sup> Electrochemical method is cost effective, however it generates copious amount of chlorine gas byproducts.

**2.4.10 Ultrasonic wave method.** The ultrasonic wave method involves the reduction of micro-ZVI particle size and increasing surface area and uniformity. It is applied in laboratories alongside other methods like chemical reduction with sodium borohydride. The process involves preparing solutions of precursor and reducing agent with ammonium hydroxide solutions and deionized water, applying ultrasonic waves through a titanium probe, and maintaining the solution temperature. The resulting nZVI is filtered, washed, and dried to avoid oxidation.<sup>108,179,180</sup> Ultrasonic method is cost effective and provides significant access to the morphological structure of nano and micro materials.

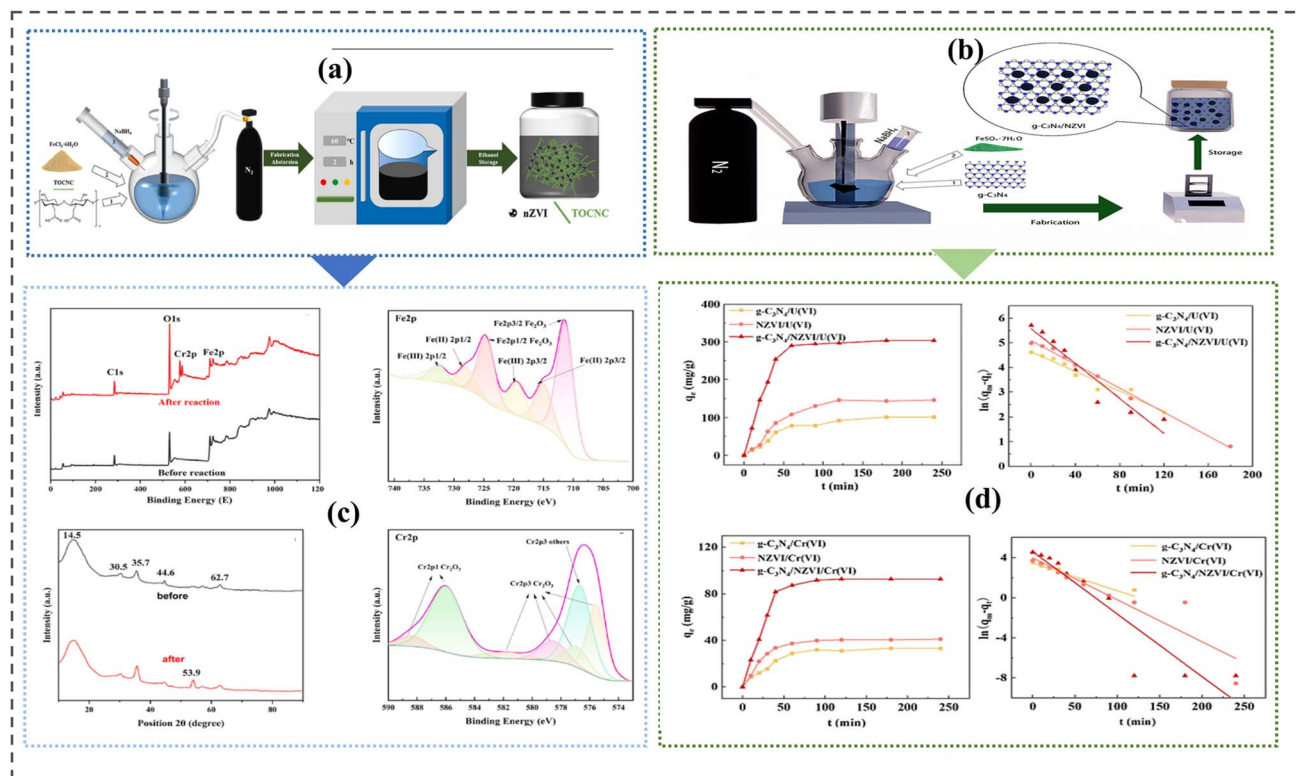


Fig. 7 One spot synthesis of nZVI nanocomposites. (a) synthesis procedure of TEMPO-oxidized cellulose nanocrystal. (c) One spot scaffolding of zero-valent iron onto graphene carbon nitride,  $\text{g-C}_3\text{N}_4$ . In both methods nanocomposites' fabrications were conducted under nitrogen gas  $\text{N}_2$  conditions to rid dissolved oxygen and maintain anaerobic conditions, TOCNC adequately adsorbed Cr(VI) due to their large surface areas and abundant active sites. Charged nZVI facilitated the conversion of adsorbed Cr(VI) to Cr(III) through the oxidation of  $\text{Fe}^0$  to  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  with adsorption rate depicted in (d). The binding energy and adsorption reaction kinetics of the zero-valent iron coupled graphene carbon nitrite are shown in (b)<sup>174</sup> Copyright: 2024, Elsevier., and<sup>154</sup> Copyright: 2023, Elsevier.





**2.4.11 Microemulsion method.** The micro-emulsion method involves the formation of uniformly dispersed inorganic phase, particle size is controlled by adjusting reaction parameters.<sup>181</sup> The reduction reaction forms an emulsion which is separated through centrifugation or magnetic methods. The average nanoparticle size depends on droplet size, iron precursor concentration, and surfactant flexibility.<sup>40</sup>

**2.4.12 Green synthesis method.** Recently, there has been increasing research interest in the green synthesis of zero-valent iron materials.<sup>182–185</sup> These methods involve utilizing plant extracts that are rich in reducing polyphenols and flavonoids components such as green tea (*Camellia Senensis*),<sup>186</sup> *Verbascum Thapsus*,<sup>185</sup> *Syzygium aromaticum* extracts,<sup>183</sup> to fabricate nano and micro-ZVI. These biobased extracts efficiently reduce Fe<sup>2+</sup> and Fe<sup>3+</sup> and other contaminants while preventing agglomeration of zero valent iron nanoparticles. In addition to being environmentally benign, green synthesis methods are efficient and cost effective (Table 1).

## 2.5 Physico-chemical properties and performance of ZVI materials synthesized through different synthesis methods

The ability of Zero-Valent Iron (ZVI) materials are emerging materials that effectively remediate a plethora of environmental

contaminants.<sup>4,53</sup> The removal performance of ZVI materials is inextricably intertwined with their physicochemical properties, which in turn is significantly influenced by the synthesis method employed.<sup>104</sup> This section provides a concise review of the enhanced removal performance of ZVI materials prepared using different synthesis techniques. Physical or top-down approaches such as the ball milling process are reported to generate ZVI particles with irregular shapes and a broad particle size distribution with an improved specific surface area due to the particle size reduction.<sup>77</sup> A study by Zhang *et al.* (2023) reported that ball-milled ZVI coupled with biochar (ZVI/BC) exhibited an improved adsorption capacity for Cr(vi) of 117.7 mg g<sup>-1</sup> at 298 K, which was 2.08 times higher than the pristine ZVI/BC. Similarly, Fang *et al.* (2022)<sup>142</sup> found that ball-milled ZVI composite showed enhanced removal of hydrophobic organic compounds (HOCs), with a maximum removal efficiency of 99%. In a combined mechanical chemical approach, the method generates ZVI particles with smaller, higher surface area, and more uniform size distribution compared to the ball milling method.<sup>133</sup> Calderón Bedoya *et al.* (2023) demonstrated that ZVI materials produced by the mechanochemical method exhibit improved reactivity and contaminant removal efficiency, along with excellent magnetic properties (55–57 emu g<sup>-1</sup>) and very low coercivity (12–19 Oe).

Table 1 Synthesis methods, methodologies, and properties of selected nano and micro ZVIs and their composites

Synthesis method/material synthesized and precursor	Methodology (with reaction conditions)	Properties of the synthesized materials	Ref
Green synthesis method nZVI particles	The procedure involved the co-addition of an optimized amounts of sodium borohydride (NaBH <sub>4</sub> ) and <i>H. caffrum</i> extract to ferric chloride (FeCl <sub>3</sub> ) under an inert nitrogen atmosphere and titration at 20 °C. Following a 30 minutes stirring period, the product was washed with deionized water and dilute ethanol (50%) and freeze-dried	Higher reactivity, stability, and well dispersed nano ZVI particles with strong Fenton catalytic properties	187
Chemical reduction method nZVI-SBA15 mesoporous silica composite	The SBA-15 silica was first prepared using sol-gel method with P123 as a structure-directing agent. Subsequently, iron was deposited onto the silica surface <i>via</i> controlled hydrolysis of iron III nitrate nonahydrate (Fe(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O). Finally, the deposited iron was reduced to zero-valent state using sodium borohydride under acidic conditions	Averaged size of nZVI-SBA15 mesoporous silica composite in the nanometre range. The material exhibited a mixed composition of iron and silica oxides, with iron content slightly exceeding 10%. The isoelectric point, influenced by the dominant silica component, was found to be around 2.0	188
Mechanochemical method Micro zero valent iron grafted nitrogen doped biochar-like graphene (mZVI/GBN composite)	10 g of reduced iron powder and NGB at a mass ratio of 10 : 1 was mixed in a stainless-steel jar with agate balls. The jar was sealed, evacuated, and purged with pure nitrogen gas three times before subjected to ball milling at 200 rpm for 12 hours using a planetary ball mill. The resulting composite was collected in a glovebox and stored in an air-proof desiccator filled with argon gas to prevent oxidation	The mZVI/NGB composite demonstrated exceptional efficiency in the removal of tetracycline TC, reaching near-complete degradation under circumneutral pH conditions (5.0–6.8), the composited displayed significant tolerance to co-existing anions such as Cl <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> and humic acid	
Combined method involving initial liquid-phase reduction Biochar incorporated nano zero valent iron (BC-nZVI composite)	Firstly, Banana peels carbonated at 250 °C for 2 h was utilized to prepare phosphoric acid-activated biochar (BC) followed by nano zerovalent iron synthesis <i>via</i> liquid phase reduction method. The nZVI-BC composite was subsequently fabricated <i>via in situ</i> formation of nZVI on the BC surface using deionized water, ferric nitrate, and sodium borohydride under nitrogen condition	Compared to microbubbles alone, tetracycline degradation performance using nano zero valent particles incorporated microbubbles or conventional microbubbles (MBs-nZVI or BC-nZVI) demonstrated significant efficiency. Removing 80% tetracycline contaminants from wastewater within 2 h	189



Ref. 147 reported the mechanochemically modified micro-ZVI material with 88.8% efficiency in the removal of phenols. In similar studies, ZVI materials were fabricated through top-down or chemical synthesis methods such as liquid-assisted pulsed laser ablation where high purity and controlled size ZVI materials are produced, resulting in a narrow particle size distribution and high specific surface area. Coincidentally, Lahoz *et al.* (2020)<sup>151</sup> reported the ZVI nanoparticles produced by this approach with polydispersity indices lower than 10 nm and 0.10, respectively, and exhibited over 99.9% performance when utilized in medicine and other environmental remediations. Another promising chemical synthesis method is the liquid-assisted chemical reduction method. This method produces ZVI nanoparticles with high chemical reactivity and dispersibility. However, there is a strong potential for agglomeration and rapid passivation when utilizing this method over time.<sup>57</sup> Other synthesis methods, such as the one-pot chemical method, electrochemical reduction, ultrasonic wave method, and microemulsion method enhance the removal performance of ZVI materials.<sup>137,174,177,181,185</sup> These methods offer various advantages, including high reactivity, controlled particle size, improved dispersion, and the use of environmentally friendly reducing and stabilizing agents. Table 2 summarizes the physicochemical properties and performance of ZVI materials synthesized *via* different synthesis methods.

### 3 Applications of nano and micro materials and environmental considerations

Nano and micro-ZVI materials have recently recorded an increasing utilization in a plethora of industries. Moreso in groundwater treatment, wastewater and environmental remediations,<sup>56,192–197</sup> degrading obnoxious and contemporary contaminants such as sulfamethoxazole<sup>198</sup> chromium,<sup>104,116,146,154,199</sup> wastewater antibiotics,<sup>200</sup> trichloroethane,<sup>109</sup> petroleum hydrocarbon, soil contamination,<sup>201</sup> lindane<sup>202</sup> nickel<sup>203</sup> arsenic<sup>204</sup> zinc, lead and cadmium contaminated soil.<sup>205–207</sup> Table 3 shows selected applications of nano and micro-ZVI and their composites in the removal various contaminants present in ground water, wastewater, soil, and other domestic and industrial effluents.

#### 3.1 Soil and groundwater remediation

Of the most dominant applications of nano and micro zero valent iron materials are in soil and groundwater remediation (see Fig. 8).<sup>3,91,155,176,192,223,232,233</sup> Their chemical reactive ability to degrade chlorinated solvents through reductive de-chlorination,<sup>65,92,134,175,228</sup> degrade nitrates,<sup>223</sup> pesticides,<sup>91</sup> micro-pollutants,<sup>176</sup> reduction of sulphides and leads,<sup>109,115,195</sup> adsorb heavy metals,<sup>22,234</sup> and organic contaminants<sup>7,9,68,95,127,186,230,235</sup> suggests a promising alternative to conventional methods.<sup>92</sup> However, factors like contaminant type, soil properties, and aging effects significantly influence their performance.<sup>84,102,103,164,214</sup> ZVI materials are particularly highly efficient in degrading metal contaminants present soil

contaminated soil.<sup>236</sup> Coincidentally, Alhadidi *et al.*, evaluated the efficiency of ZVI materials in the remediation of metal based contaminated soil, the results revealed 80% removal efficiency for various metals categorized by the Nieboer–Richardson method.<sup>237</sup> Similar and better performance ZVI materials in soil remediations is also reported.<sup>238</sup>

However, despite this promising performance and applications of ZVI materials, it is imperative to assess their impact on soil microorganisms when applied for soil remediations. Interestingly, Saccà *et al.*, (2014) coupled molecular and classical methods to investigate the impact of nano zero valent materials on soil microorganism, from their findings, classical toxicity tests using nematodes (*Caenorhabditis elegans*) revealed no negative effects of nano ZVI on microorganisms. However, molecular analysis of soil microbial communities showed significant changes in gene expression associated with nano ZVI materials exposure.<sup>239</sup> Interestingly, following their conclusion, these gene expressions changes of soil microorganisms varied depending on soil characteristics, hence highlighting the need for case-by-case evaluation. Generally, potential environmental risks associated with iron oxide formation and unintended contaminant mobilization necessitate a thorough evaluation before large-scale application.<sup>240,241</sup>

#### 3.2 Water treatment

Contemporary challenges posed by emerging contaminants in water sources presents a new frontier for nano and micro zero valent iron materials. ZVI materials have showed potentials for removing pharmaceutical waste,<sup>71,176,242</sup> and pesticides<sup>91,103</sup> washed and transported to water bodies by rain or through municipal effluents.<sup>242,243</sup> Surface modification strategies can further enhance their selectivity and efficiency for targeted contaminant removal.<sup>71,244,245</sup> Liu *et al.*, investigated the effectiveness of zero-valent iron (ZVI) for removing phycocyanin from water. The results revealed more than 80% removal efficiency in acidic environments, further analysis proposed two reaction mechanisms *viz.* adsorption onto the ZVI surface and coagulation by iron ions released from ZVI materials.<sup>100</sup> Like ZVI materials' applications in soil remediations, significant challenges remain, particularly in ZVI materials' separation and regeneration after water treatment operations, hence, limiting their widespread applications.

#### 3.3 Industrial catalysts

Nano and micro-ZVI materials as catalysts for hydrogen production from water splitting or hydrolysis reactions is a sustainable route towards clean energy generation.<sup>246</sup> ZVI materials offer benefits in terms of their cost and material abundance compared to conventional catalytic materials.<sup>247</sup> Chen *et al.*, explored the potential of nano and micro-ZVI materials for hydrogen production, their results revealed nano-ZVI to exhibit significantly higher iron-normalized hydrogen production rates of 15.2–58.3 mg<sub>H<sub>2</sub></sub> kg<sub>Fe</sub><sup>-1</sup> h<sup>-1</sup> compared to their Micro-ZVI counterpart. Interestingly, doping nano-ZVI with 1% noble metals *viz.* Pd, Ni, Cu, or Ag was observed to further accelerates hydrogen production from 2–39



Table 2 Comparison of physico-chemical properties and performance of ZVI Materials synthesized through different synthesis methods

Synthesis method	Material physico-chemical properties	Removal performance	Reference
Mechanical ball milling	ZVI particles with irregular shapes and broad size distribution High specific surface area due to particle size reduction potential for agglomeration and loss of reactivity	Ball milled ZVI/BC recorded an improved adsorption capacity for Cr(vi) to 117.7 mg g <sup>-1</sup> (298 K), 2.08 times higher than the pristine ZVI/BC	190
Mechanochemical method	ZVI particles with smaller and more uniform size distribution  Higher specific surface area compared to ball milling	The method produces ZVI materials with improved reactivity and contaminant removal efficiency  The method produces ZVI materials with excellent magnetic properties (55–57 emu g <sup>-1</sup> ) and very low coercivity (12–19 Oe)	133
Liquid-assisted pulsed laser ablation	ZVI nanoparticles with high purity and controlled size Narrow particle size distribution and high specific surface area	Produces ZVI materials with polydispersity indices lower than 10 nm and 0.10, respectively >99.9% performance for medicine and environmental remediation	151
Liquid-assisted chemical reduction	ZVI nanoparticles with high reactivity and dispersion Potential for agglomeration and loss of reactivity over time	ZVI coupled zinc incorporated silica bn titania dioxides synthesized <i>via</i> chemical reduction method showed >99.8% arsenic removal at 5.0 mg L <sup>-1</sup>	191
Gaseous chemical reduction	Controlled particle size and morphology through gas-phase reactions Generates ZVI particles with high purity but high environmental impacts	The size of zero valent iron materials synthesized <i>via</i> this method are approximately 60 nm with significantly controlled morphologies	150
Carbo-thermal reduction	ZVI particles with high purity, crystallinity with exceptionally high chemical reactivity and regenerative capacity Potential for carbon contamination and agglomeration	The nZVI@MOF-CN demonstrated significant reactivity achieving bromate reduction efficiency of 80% after five successive regeneration cycles	249
One-pot chemical method	ZVI nanoparticles with high reactivity and dispersion Relatively simple and scalable synthesis process Potential for agglomeration and uncontrolled particle size distribution	The sequestration of U(vi) and Cr(vi) by NZVI nanocomposite was greater than that of pure NZVI or g-C, demonstrating a significant enhancement in the performance of NZVI composites	39
Electrochemical reduction	ZVI nanoparticles with high purity and controlled size Enables <i>in situ</i> generation and application of ZVI	Moratalla <i>et al.</i> , reported zero-valent iron (ZVI) facilitated conversion of 95% iopamidol into C <sub>17</sub> H <sub>25</sub> N <sub>3</sub> O <sub>8</sub> with nearly total elimination after electrolysis of the initial pollutant	177
Ultrasonic wave method	ZVI nanoparticles with high specific surface area Improved dispersion and reactivity compared to conventional methods	99.76% of Rh B degradation within 12 min at Ph 4 and 1.0 g per L ZVI concentration	137
Microemulsion method	ZVI nanoparticles with controlled size and narrow distribution Enhances stability and dispersibility of ZVI in aqueous media	Produce nanoparticles with exceptional superparamagnetic and ferromagnetic properties	181
Green synthesis method	Utilizes environmentally friendly reducing and stabilizing agents Generates ZVI nanoparticles with high purity and biocompatibility	Enhanced performance and complete reduction of Cr(vi) after 30 min under 1 g per L green synthesized nZVI	185

times, with Pd–Fe<sup>0</sup> achieving optimal rate of 1490 mg<sub>H<sub>2</sub></sub> kg<sub>Fe</sub><sup>-1</sup> h<sup>-1</sup>. Nano ZVI materials system is cost effective and operates under ambient conditions with superior volumetric hydrogen storage density (279 kg<sub>H<sub>2</sub></sub> m<sup>-3</sup>) compared to conventional catalytic materials.<sup>247</sup> However, their efficiency and long-term stability require significant improvement,<sup>247,248</sup> for crucial economic viability, developing efficient regeneration and separation strategies of nano- and micro- ZVI materials after use in industrial processes is highly essential.

### 3.4 Industrial wastewater effluents

Nano and micro materials are emerging materials in degrading organic and inorganic obnoxious pollutants present in pharmaceuticals,<sup>71</sup> and other industrial wastewater streams for cleaner engineering processes.<sup>249–252</sup> Zhang *et al.*, evaluated the suitability of ZVI materials in the remediation of Swine wastewater (SWW), high removal efficiency was observed at acidic pH (3) and in the presence of dissolved oxygen.<sup>253</sup> However, similar





**Table 3** Selected applications of nano and micro-ZVI materials

Type of contaminant	Type of zero valent iron material	Efficiency in contaminants removal and conditions	Remediated material	Ref.
Uranium, U(vi)	Fe-PANI-GA (zero-valentiron-polyaniline graphene aerogel)	Excellent reduction of U(vi) in acid solutions through sorption and partial precipitation	Aqueous solution containing radionuclide pollutant, U(vi)	208
Uranium, U(vi)	Fe-Ni/graphene; nZVI loaded chitosan (NZVI/CS); Fe-Cu/MBC; Fe-Cu	Maximum sorption and reduction of U(vi) with maximum removal capacity	Uranium contaminated wastewater	209–211
Chromium	Sulfidized nZVI supported Oyster shell powder	Excellent performance, Cr(vi) removal capacity of 164.7 mg g <sup>-1</sup> in acidic solution	Wastewater	212
Oxytetracycline (OTC)	Dry and wet Pre-ZVI-activated peroxymonosulfate (PMS)	Varying the pH values (3,7 and 9). Both dry and wet Pre-ZVI/PMS systems achieved high initial OTC removal efficiency (>43%) at pH 3 Long-term OTC degradation was significantly lower for Pre-ZVI/PMS (8–9%) compared to PMS alone (44%) Further research is needed to improve the long-term effectiveness of Pre-ZVI/PMS for organic matter removal	Organic matter contaminated water	107
Trivalent and pentavalent antimony (Sb)	Sulfidated nano zero valent iron coupled with graphene oxide (S-nZVI@GO)	Varying pH from (3–9), excellent contaminant removal of 96.7% under aerobic condition with adsorption capacity of Q <sub>max</sub> = 311.75 mg g <sup>-1</sup>	Sb contaminated wastewater	110
Orange II sodium salt (OR2)	Green synthesized zero valent iron (gNZVI)	Inert (nitrogen) controlled environment, 65% 20 ppm OR2 dye degradation in 1 hour, with excellent Fenton catalytic properties	For dye removal such as in textile wastewater (effluent) treatment	187
Xenobiotics	nZVI-SBA-SiO <sub>2</sub>	Acid controlled polymer reaction, promising properties with high xenobiotics degradation potential	Xenobiotics contaminated groundwater and wastewater	188
Copper ions	Core-shell zero valent iron, CS-nZVI	For batch process, adsorption of copper ions was significantly controlled by the operational parameters however, CS-nZVI recorded high efficacy in treating copper ions contaminated water	Wastewater	70
Lead (Pb)	Nano zerovalent iron, nZVI coupled low molecular weight organic acid	Lead removal rate of 64% and 83% with rapid adsorption rate in 4 hours. Efficiency decreases with increasing pH		84
Metal and/or metalloids contaminants; Cu(II), Zn(II), Cr(VI), and As(V)	Nano zerovalent iron	Removal efficiency varied depending on the interaction mechanisms and solution speciation while increasing the ionic strength decreased the rate of removal	Hydraulic fracturing wastewater, saline wastewater	213
Arsenic (As)	Goethite nanospheres(nGoethite) coupled nano zero valent iron (Nzvi)	nGoethite and nZVI effectively immobilized As in the tested brownfield soil with an 89.5% decrease in As concentration however, high concentration of Goethite nanospheres increase the phytotoxicity of the polluted soil	Arsenic polluted soils	161
DDT (1,1,1-trichloro-2,2-bis(p-chlorophenyl) ethane)	Nano zero valent iron	nZVI treatment degraded 50% of 20 mg DDT contaminants in the spiked sandy soils and 24% degradation in 24 mg aged DDT contaminated soil	DDT-polluted soil and spiked sandy soil	214

Table 3 (Contd.)

Type of contaminant	Type of zero valent iron material	Efficiency in contaminants removal and conditions	Remediated material	Ref.
Trinitrolycerin (TNG)	Nano zero valent iron and nZVI supported nanostructured silica SBA-15	ZVI-nanoparticles and ZVI-nanoparticles/SBA-15 efficiently degrade TNG in water, resulting in the production of glycerol and ammonium with respective normalised rate constant of 0.36 and 0.33 L h <sup>-1</sup> m <sup>-2</sup>	Trinitrolycerin (TNG) contaminated soils and water	215
Direct black G (DBG), a model azo dye	Kaolin supported nanoscale zero-valent iron, K-nZVI	Excellent degradation efficiency with mechanisms involving prompt adsorption of DBG onto the K-nZVI surface and the subsequent oxidation of DBG by hydroxyl radicals at the K-nZVI surface	Wastewater containing azo dyes	216
1,1,1-Trichloro-2,2-bis(p-chlorophenyl) ethane or (DDT)	nZVI, produced through chemical reduction method using precipitation with borohydride, and nZVI, produced through gas phase reduction of iron oxides under H <sub>2</sub>	Both types of nZVI effectively degraded DDT in water but were slow in the remediation of DDT contaminated soils	DDT contaminated water and soils	217
Hexavalent chromium (Cr(vi))	Nano-zero-valent iron (ZVI) encapsulated in a carbon shell (ZVI-C)	pH and concentration of the contaminant (Cr(vi)) influenced the electron utilization efficiency of ZVI and the utilization efficiency was observed to increase up to 80% at 2000 mg per L Cr(vi)	Cr(vi)-contaminated wastewater	118 and 218
<i>Escherichia coli</i> ( <i>E. coli</i> )	Sulphur modified nano zero valent iron (S-nZVI)	ZVI-C shielded ZVI from the acidic conditions and the formation of undesired precipitates	Groundwater	219
Dewaterability of aerobic digested sludge	Persulfate combined ZVI (PS-ZVI)	Reduced toxicity of zero valent iron materials used ground water treatments, although other ions presence in ground water could interfere with the reactions, however coupling sulphur to nano ZVI was observed to lose inherent toxicity over time	Sludge	220
Tetracycline contaminants	Biochar supported nano ZVI	Persulfate combined zero valent iron technique recorded 80% reduction in capillary suction time (CST), with an efficient removal of hydrophilic organics compounds (HOC) presence in extracellular polymeric substances (EPS)	Wastewater	189
Chromium(vi)	Zero valent iron biochar (ZVI-BC) composite	Micro-nanobubbles supported nano zero valent iron (MBs-nZVI composite) recorded 80% tetracycline degradation within 2 h from wastewater effluent which was significantly greater compared to the tetracycline degradation efficiency <i>via</i> microbubbles alone	Chromium contaminated soil	125





Table 3 (Contd.)

Type of contaminant	Type of zero valent iron material	Efficiency in contaminants removal and conditions	Remediated material	Ref.
DDT and DDT byproducts	Zero valent iron coupled EDTA, (ethylenediaminetetraacetic acid)	Fenton-like system efficiently remediated DDT contaminated soils while an increase in reactants concentrations (EDTA and ZVI) significantly increased the efficacy of DDT degradation as well as the removal of DDT byproducts contaminants with a risk of the production of secondary pollutants at excess DDT concentrations	Soil contaminated with dichlorodiphenyltrichloroethane and its reaction byproducts	221
Trichloroacetic acid from family of Halo acetic acids or simply HAAs	ZVI encapsulated biological active carbon (Fe0-BAC)	Fe0-BAC completely removed TCAA and its byproducts, dichloroacetic acid (DCAA) and monochloroacetic acid (MCAA) contaminants through combined chemical dehalogenation and biodegradation of ZVI and BAC	Wastewater, halogenated/chlorinated drinking water, and swimming pool water	222
Nitrate contaminants	Nano magnetite supported zero valent iron	Nano-sized magnetite substantially improved nitrate reduction in groundwater. The rate of nitrate reduction increases proportionally with the loading of magnetite nanoparticles. The presence of magnetite nanoparticles aids electron transport from Fe0 to adsorbed nitrate, thus supporting the reduction process	Ground water	223
Nitrate contaminants	Nano zero valent iron	Removal efficiency of nitrate contaminants of over 90% using laboratory scale continuous flow systems	River and ground water	224
Thiobencarb contaminants	Zero valent iron powder	Through reduction and adsorption ZVI effectively treated 10 ml sample solution containing 10 µg ml <sup>-1</sup> of thiobencarb at room temperature for 12 hours	Thiobencarb contaminated water/wastewater	105
Uranium, copper, and cadmium	Nano zero valent iron	Zero valent nanoparticle efficiently degraded the studied contaminants. The efficiency increases with increase and reduction of pH and oxidation–reduction potential	Acid mine water	225
Arsenic, copper, and other heavy metals	Nanoparticles zero valent iron	High removal capacity to over 99.5% of arsenic and copper using gravitational separation and zero valent nanoparticles recirculation process	Heavy metals contaminated wastewater	113
2,2,0,5,50-Tetrachlorinated biphenyl (PCB-52)	Zero valent iron encapsulated anionic/cationic surfactants	The higher the concentration of surfactants the greater efficiency and the more the reduction of PCB-52 contaminants	Soil and/or sediment solutions	226
Nitrate and total nitrogen	Zero valent iron nanoparticles coupled activated carbon (nZVI-AC)	Total nitrogen removal efficiency proportionately increased with an increase in nZVI/AC concentration but declined above 2 : 1 nZVI/AC ratio. When utilized alone, nZVI recorded 100% nitrate removal while its efficacy in terms of total nitrogen (TN) was virtually the same at about 35% at acidic pH like nZVI/AC composite	Nitrate contaminated ground water	227

Table 3 (Contd.)

Type of contaminant	Type of zero valent iron material	Efficiency in contaminants removal and conditions	Remediated material	Ref.
Chlorinated dense non-aqueous phase liquids, DNAPLs	Zero valent iron nanoparticles coupled polyethyleneimine PEIe/nZVI	Significant transformation of DNAPLs contaminants into non-toxic elements. The reduction reactions with contaminated ground water occurred prior to the oxidations of nano zero valent iron composite	Contaminated groundwater	228
Nitrobenzene, NB	Zero valent iron nanoparticles supported ordered mesoporous carbon (nZVI/OMC)	nZVI/OMC composite exhibited enhanced removal efficiency, which was attributed to its combined adsorption and synergistic reduction properties towards nitrobenzene	Wastewater and groundwater	121 and 229
Organic pollutants (azo-dye orange II)	Nanoscale zero valent iron	Significant formation of iron oxide/hydroxide layers on the nZVI surface, and the adsorption of the pollutant and its intermediates. Rapid decolorization of orange II with nZVI, but the removal of total organic carbon (TOC) observed was slower, with maximum removal achieved at pH 9.0	Wastewater	230
Copper	Zero valent iron, ZVI	Cu removal was quick and efficiently completed at pH 2–5. Complete Cu removal was achieved within 35 minutes at pH 4 for Cu loadings ranging from 0.393 to 4.72 mM. The concentrations of Cu <sup>2+</sup> and dissolved oxygen were found to be strongly connected	Wastewater	231
Organophosphate pesticides	Zero valent iron	Complete removal of toxicity with rapid degradation of malathion, ethyl parathion and methyl parathion	Groundwater	91
Phycocyanin	Zero valent iron	High phycocyanin removal at pH value below 6 which decreases as pH increased. The removal efficiency and mechanism were governed by the coagulations of the dissolved ZVI ions as compared to the conventional adsorption mechanism where contaminants are adsorbed on material surface	Drinking water	100



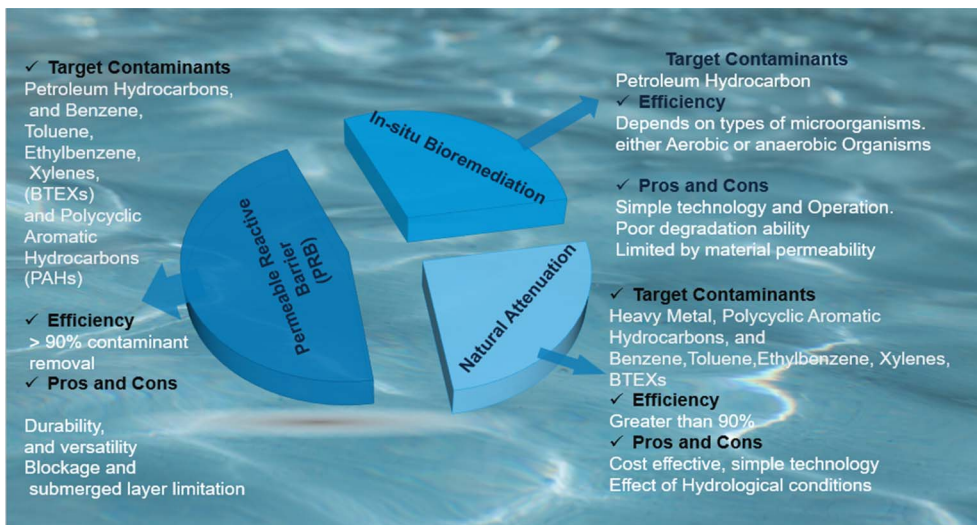


Fig. 8 Nano and micro-ZVI Materials' applications in groundwater remediation *in situ* technologies, pros and cons, and their target contaminants.

studies on the engineering applications of these novel materials recommended optimizing materials' particle size and surface properties for efficient pollutants degradation and improved catalytic selectivity.<sup>55,254,255</sup>

### 3.5 Organic pollutant removal

Nano and micro-ZVI materials degrade various organic pollutants present in industrial wastewater streams, such as dyes, pharmaceuticals, and pesticides (see Table 2). These pollutants can be harmful to ecosystems if released untreated.<sup>108,256</sup> The degradation reaction mechanism involves nano and micro-ZVI materials acting as a reducing agent, and hence breaking down the complex organic molecules into simpler and less harmful compounds.<sup>241</sup>

**De-sulfurization:** Although there is barely any study with direct application of nano and micro-ZVI materials for removing sulphur impurities from fuels, potential utilization of these materials when coupled with other materials could contribute to cleaner fuel combustion.

### 3.6 Potential engineering applications

**3.6.1 Battery technology.** Future research should explore the potential of utilizing nano and micro-ZVI materials as anodic material in lithium-ion batteries considering their high physicochemical and theoretical capacity for lithium storage. Challenges to overcome could include overcoming volume changes during charge/discharge cycles and improving electrode stability.

**3.6.2 Sensors.** The distinguished reactivity and surface properties of nano and micro-ZVI materials make them potential materials for developing sensitive and selective sensors for wide process engineering applications.

**3.6.3 Biomedical applications.** Emerging research should investigate the potential of nano and micro-ZVI materials in biomedical engineering applications like biocatalysis and

targeted drug delivery considering their biocompatible modifications and efficacy in pharmaceuticals. However, comprehensive toxicity assessment is highly essential for safe biomedical utilization.

**3.6.4 Construction materials.** Nano and micro-ZVI materials can be incorporated into building materials to enhance their fire resistivity or conductivity. However, the long-term stability, and durability, of such materials need further investigation.

### 3.7 Environmental considerations

Despite the promising and versed applications of these emerging materials significant efforts need to be placed in evaluating their environmental implications and detrimental effect on both human, animal, and aquatic lives. Since chemical methods for synthesising nano and micro-ZVI materials involve the use of various reagents, such as iron chloride,<sup>70,187</sup> sodium borohydride, and iron sulphate,<sup>257</sup> as well as gases like; argon,<sup>258</sup> nitrogen,<sup>259</sup> and hydrogen.<sup>260</sup> These reagents have reported environmental impacts due to their production and can result in waste, wastewater, and emissions containing these compounds. Some of these compounds, such as sodium borohydride, isooctane, polyvinylpyrrolidone, cetylpyridinium chloride, and sulphur pose risks to human health and the environment.<sup>261</sup> Water consumption in most methods is low, but the ultrasonic wave method has a high-water consumption rate. Wastewater generation is directly related to water consumption, with methods like chemical reduction with sodium borohydride, micro-emulsions, and ultrasonic waves generating more wastewater byproducts. The wastewater contains chemical components that can be hazardous, requiring proper treatment before reuse or disposal.<sup>262</sup> Energy consumption is another important factor in process engineering applications, with gas reduction using hydrogen gas and the ultrasonic wave method having high energy





consumption (refer to Section 2). High energy consumption contributes to environmental impacts, including resource use, gas emissions, and climate change. The composition of the energy matrix also affects the environmental impacts, with countries relying more on renewable energy sources experiencing lower impacts. Solid waste generation is primarily associated with filtration processes, where the filter used may contain chemical compounds from the process reagents. Proper treatment, such as incineration, is necessary before final disposal.

## 4 Conclusions and future perspectives

In conclusion, nano and micro-ZVI materials, and synthesis methods coupled with their multifaceted applications are concisely reviewed herein. The crucial points are summarized as follows.

### 4.1 Synthesis strategies

A diverse range of nano- and micro-ZVI materials synthesis methods were reviewed, each with distinct advantages and limitations. Selecting the optimal method depends on factors like the targeted production scale, economic feasibility, technological requirements, and desired nano- and micro-ZVI material characteristics. Future research should prioritize optimizing existing methods, exploring eco-friendly approaches, and evaluating their industrial applicability. Table 2 provides an insight into recent methodologies of selected synthesis methods with their recorded efficiencies and the properties of the synthesized materials to serve as a reference in the selection process.

### 4.2 Tuning synthesis methods for specific engineering applications

Selection of the right synthesis method for a given nano and micro-ZVI materials' properties requirement and particular engineering application is highly crucial for ensuring the efficacy of the fabricated nano and micro-ZVI materials in process operations. This review found that by tuning nano and micro-ZVI materials properties such as size and morphological structures researchers can enhance material performance, selectivity, and catalytic activity. The smaller the particle size, the higher the surface area, and the greater the contaminant's adsorption. Other findings revealed that modification of material surface properties enhances the stability of nano and micro ZVI materials, hence improving their prospects in a plethora of engineering applications. pH, concentration, and temperature, among other factors, are found to proportionately influence overall ZVI materials performance (X. Sun *et al.*, 2015).

### 4.3 Environmental remediation

Nano and micro-ZVI materials are unveiled to act as highly effective materials for soil, groundwater, and wastewater remediations, effectively degrading organic pollutants, heavy

metals, and other emerging contaminants (see Table 3) through reductive degradation and adsorption processes.

### 4.4 Challenges

Despite the invaluable potential of nano and micro-ZVI materials, contemporary challenges persist in their utilizations in many areas. These challenges revolve around three key factors *viz.* aggregation, selectivity, and potential environmental impacts.

**Improved Stability and applicability:** investigating sustainable strategies will help in mitigating material aggregation and improve their stability for diverse environmental utilization, particularly *via* modification of morphological structure or encapsulation with other supportive materials. Additionally, synthesizing stable nano and micro-ZVI materials with improved multifunctional surface properties can widen the prospective applications of these novel materials beyond environmental remediations such as energy storage, drug delivery, and sensing materials in electronics devices as well as magnetics materials thereby extending and utilizing the full potential of these emerging materials.

**Combined technologies:** integrating nano and micro-ZVI technologies with other engineering techniques, such as electrocatalysis or bioremediation can help foster the establishment of synergy in developing a robust environmental remediation system.

**Life cycle assessment:** performing comprehensive life cycle assessments to gauge the environmental impact and sustainability of nano and micro-ZVI materials production, utilization, and environmental limitations is highly essential for sustainable industrial applications.

**Regulatory frameworks:** like all other engineering materials, determining clear standards and protocols for the safe and responsible utilization of these materials to warrant environmental protection against waste generation, waste disposal, and community health is crucial.

Therefore, by concentrating on these outlined fundamental features, nano and micro-ZVI materials and their synthesis technologies would uncover a sustainable and transformative means of environmental remediation systems coupled with resource recovery, and the development of advanced materials.

## Conflicts of interest

There are no conflicts to declare.

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