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An efficient catalytic degradation of trichloroethene in a percarbonate system catalyzed by ultra-fine heterogeneous zeolite supported zero valent iron-nickel bimetallic composite

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Abstract

Zeolite supported nano iron-nickel bimetallic composite (Z-nZVI-Ni) was prepared using a liquid-phase reduction process. The corresponding surface morphologies and physico-chemical properties of the Z-nZVI-Ni composite were determined using scanning electron microscopy (SEM), transmission electron microscopy (TEM), Energy dispersive X-ray spectra (EDS), Brunauer Emmett Teller (BET) adsorption, wide angle X-ray diffractometry (WA-XRD), and Fourier transform infrared spectroscopy (FTIR). The results indicated high dispersion of iron and nickel nano particles on the zeolite sheet with an enhanced surface area. Complete destruction of trichloroethene (TCE) and efficient removal of total organic carbon (TOC) were observed by using Z-nZVI-Ni as a heterogeneous catalyst for a Fenton-like oxidation process employing sodium percarbonate (SPC) as an oxidant. The electron spin resonance (ESR) of Z-nZVI-Ni verified the generation and intensity of hydroxyl radicals (OH[•]). The quantification of OH[•] elucidated by using *p*-chlorobenzoic acid, a probe indicator, confirmed the higher intensity of OH[•]. The transformation products were identified using GC-MS. The slow iron and nickel leaching offered higher stability and better catalytic activity of Z-nZVI-Ni, demonstrating its prospective long term applications in groundwater for TCE degradation.

Graphical abstract

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Compliance with Ethical Standards

The authors declare that they have no conflict of interest.

Keywords

Trichloroethene (TCE); heterogeneous Fenton catalyst; sodium percarbonate (SPC); Z-nZVI-Ni; groundwater remediation

1. Introduction

Chlorinated organic solvent compounds such as trichloroethene (TCE) continue to pose significant problems as groundwater contaminants due to their recalcitrant nature and ubiquitous distribution in industrialized regions. The exposure of TCE can cause threats to human beings due to its carcinogenic and cytotoxic effects that can cause severe damage to central nervous system, endocrine system and immune system. The use of advanced oxidation processes have been employed recently for the remediation of groundwater contaminated by chlorinated solvents and other compounds. In-situ chemical oxidation (ISCO) using persulfate, potassium iodate, calcium peroxide, potassium permanganate, and homogeneous Fenton reagent has been studied comprehensively for the remediation of soil as well as groundwater [1–6]. The higher catalytic capacity of the homogeneous Fenton reagent through the generation of hydroxyl radicals ($\text{OH}^\bullet$) having a redox potential of 2.76V is a significant advantage. However, the Fenton process involves specific activation of the transformed functional groups due to weak oxidizing capability of the non-activated peroxide. The usage, transportation, and storage of the homogeneous Fenton reagent in its concentrated form is not desirable due to safety reasons. In addition, strong dependence on pH (optimal performance at pH 3.0), loss of catalyst and injection well plugging limits its application. Research is ongoing to develop a safer, less expensive catalyst for large scale applications [7].

Recently, sodium percarbonate (SPC) has received considerable attention as a selective, efficient and environmental friendly oxidant. SPC is a solid per-oxygen compound that is relatively stable, non-toxic, easily handled, and relatively inexpensive, being used in large scale industrial applications, primarily as antiseptic and bleaching agent in detergents [8–9]. SPC is a peroxyhydrate, primarily functioning as a convenient source of hydrogen peroxide (H_2O_2). SPC produces percarbonate species $[\text{HOOC}(\text{O})\text{O}]^-$ in aqueous media that may be expected to behave as an electrophile [9–10].

SPC can be activated through the use of transition metals such as iron as shown in the subsequent reactions Eqs. 1–3 [2, 10–11].

Upon mixing of SPC in aqueous media, the pH of the solution increases, acting as a buffering agent against the pH reduction associated with peroxide-induced oxidation [12–15]. Thus, in contrast to peroxide, a major advantage of using SPC for ISCO application is that it is effective over a relatively wide range of pHs [13, 14]. In addition, the SPC decomposition products are non-toxic to micro-organisms owing to its compatibility with bioremediation.

The use of nano zero valent iron (nZVI) has been applied successfully in Fenton like processes for the generation of hydroxyl radicals instead of Fe^{2+} or Fe^{3+} for the in-situ groundwater remediation technologies [16–18]. The nZVI has gained much attention in decontaminating the environmental pollutants due to its higher specific surface area and increased reactivity [17]. However, there are still some drawbacks associated with the usage of nZVI for the process that needs to be addressed. For instance, the nZVI coalesce into aggregation [19] by generating an oxide or hydroxide layer on its surface by reducing its catalytic ability [20]. The filtration is also required for the removal of nZVI particles at the end of the treatment, i.e. separation from the waste stream. Moreover, the targeted contaminants must diffuse through the surface of the nZVI to reach the available active sites before their degradation [21].

Heterogeneous Fenton like catalysts have been employed as an effective alternative to the conventional homogeneous Fenton catalysts to mitigate the above drawbacks efficiently. The more efficient and more stable characteristics are the desirable tasks to achieve in the case of heterogeneous Fenton like catalysis. Various heterogeneous solid catalysts including iron-loaded natural zeolite [16, 22] and iron oxides (goethite, magnetite, hematite, and ferrihydrite) [23] have been employed to activate hydrogen peroxide for the generation of reactive oxygen species (ROS).

Further efforts were made that led towards the development of bimetallic catalysts for the remediation of chlorinated organic solvents [24]. The incorporation of second metal increased the stability and catalytic reactivity of the catalyst and decreased the toxic products accumulation [25]. For example, Wu found that iron and nickel bimetallic nano particles (NPs) supported on cellulose acetate (CA) presented an efficient and promising role

in the removal of TCE from water [20]. Feng and his colleagues also demonstrated a remarkable increase in degradation of TCE by preparing bimetallic NPs on starch based support [26]. Schrick showed improved TCE degradation using high surface iron and nickel bimetallic NPs by increasing the reaction rate and absence of toxic products [27]. The incorporation of bimetallic iron and nickel NPs on chitosan as a stabilizer was effectively used for the removal of the mixed amoxicillin and cadmium from the aqueous solution [28]. Genetically engineered acetylcholinesterase (AChE) immobilized in poly (vinyl alcohol)/Fe–Ni alloy nanocomposite has shown better performance for the detection of phosmet [29]. Similarly, polyethyleneimine-decorated graphene oxide supported Fe-Ni demonstrated excellent dehydrogenation [30].

The increased reactivity of the bimetallic catalysts can be achieved by using some suitable support materials as described above [31]. For instance, reduced graphene oxide [32], multi walled carbon nano tubes [33], mesoporous carbon [24], activated carbon [23], and mesoporous silica [34] have been frequently used as support materials in literatures. It is need of the era to find some new materials that can be used effectively as support materials in synthesis of the bimetallic catalysts and their applications. In this study, a novel support, i.e. natural zeolite was chosen as a supporting material for bimetallic iron and nickel NPs due to its relatively lower cost, convenient commercial accessibility, and positive characteristics (e.g., adsorption capability, chemical resistance, and thermal stability) and its application was tested in groundwater contaminant abatement which were never discussed in literature before.

The novelty of this study lies in synthesis of zeolite-supported iron and nickel bimetallic NPs as heterogeneous catalyst for SPC-based oxidation for the degradation of TCE as a model groundwater contaminant. As expected, the synthesized composite (Z-nZVI-Ni) offered higher surface area, more active sites, slow leaching of iron and nickel particles, exceptional stability and higher reactivity indicating the significance of Z-nZVI-Ni as a heterogeneous catalyst. The role of Z-nZVI-Ni was elucidated for TCE degradation by measuring adsorption rates, production of hydroxyl radicals, stability, kinetics and reusability of the Z-nZVI-Ni. Multiple characterization methods were employed to elucidate the governing mechanisms.

2. Materials and methods

2.1 Preparation of the zeolite-supported iron-nickel bimetallic nano-composite

The zeolite-supported iron-nickel bimetallic nano composite (Z-nZVI-Ni) was prepared using a liquid-phase reduction process. Briefly, ferrous sulfate heptahydrate (5.0 g) and nickel chloride hexahydrate (0.05 g) were dissolved in 250 mL of ethanol and ultra-pure water with a 2:1 volume ratio. Natural zeolite (2.5 g) was then added into the solution. The solution pH was adjusted near 4.0 to avoid the possible oxidation of iron and nickel and to maintain stability of the zeolite. The suspension was sonicated for 20 min and then vigorously stirred for 30 min to obtain a homogeneous mixture. The solution pH increased slightly due to the hydrolysis of zeolite but remained below 5.0. Sodium borohydride (1.0 M, 50 mL) was added dropwise (2.0 mL/min) into the stirred suspension to enhance

reduction of both metals, resulting in the formation of blackish solid particles through the reactions as shown in Eqs. 4–5.

This process was carried out in a nitrogen environment to avoid any unwanted consequences. The suspension was continuously stirred for further one hour to ensure the completion of the redox reactions. Finally, the black particles were vacuum filtered using filter paper (diameter = 47 mm, pore size = 0.45 μm) and then rinsed twice with deionized water and ethanol respectively. These particles were dried under vacuum overnight at 70°C. Zeolite-supported nano iron-copper (Z-nZVI-Cu), zeolite-supported nano zero valent iron (Z-nZVI), unsupported nano zero valent nickel (nZV-Ni), and unsupported nano zero valent iron (nZVI) were also prepared using the same method for the purpose of comparison.

2.2 Characterization of zeolite supported iron-nickel bimetallic nano-composite

The corresponding surface morphologies of zeolite and Z-nZVI-Ni were acquired by using scanning electron microscopy (SEM, JSM-630LV, Tokyo, Japan) and transmission electron microscopy (TEM, JEM-2100 electron microscope operated at an accelerating voltage at 200 kV). The characteristics of diffraction patterns were recorded by X-ray diffractometer (XRD) along with Rigaku D/max diffractometer (2550 VB/PC; $\text{CuK}\alpha$ ($\lambda = 0.154$ nm radiation)). Brunauer–Emmett–Teller (BET) method (Quantasorb Jr. Instrument Quantachrome Co. UK) was used to obtain nitrogen adsorption-desorption isotherms to measure particle size, total pore volume, pore size, and specific surface area of the zeolite and Z-nZVI-Ni. Fourier transform infrared spectroscopy (FT-IR) (Nicolet 6700, Thermo Fisher Scientific, 4000–400 cm^{-1}) with a scan number of 32 and spectral resolution of 4 cm^{-1} was used to characterize the chemical bonding environment. The calcination of potassium bromide (KBr) was achieved at 600°C for 360 min in a muffle furnace to remove any possible organic impurities before testing. Energy dispersive X-ray spectroscopy (EDS) was used to determine the elemental composition of the zeolite and Z-nZVI-Ni.

2.3 Experimental procedures

The standard solution of TCE (0.15 mM) was prepared by allowing pure non-aqueous phase liquid (TCE) to equilibrate with milli-Q water for one hour with moderate stirring. All the catalysts were vacuum dried at 100°C before use in experiments. The adsorption-desorption equilibrium between TCE and catalysts was achieved by stirring the suspension vigorously for 60 min without the addition of SPC. The tests regarding degradation of TCE were carried out in a cylindrical glass reactor of volume (250 mL) having two openings at the top. The glass reactor has inner diameter of 6.0 cm and height of 9.0 cm with one opening at the top of the reactor for dosing purposes and the second opening for sampling purposes. A

temperature of $20 \pm 0.5^\circ\text{C}$ was maintained by means of circulation of the external thermostatic water in the double jacket of the reactor by using temperature bath (DC Ningbo, China). A magnetic stirrer covered with Teflon was also inserted into the reactor for mixing of the reagents with subsequent addition of all the reagents. The solution pH was maintained by using HCl (0.1 M) and recorded with pH meter.

The degradation performance of a probe indicator (*p*-chlorobenzoic acid) was evaluated by using high performance liquid chromatography (HPLC) to quantify hydroxyl radicals in our system. Aqueous samples were collected at set time intervals. The samples were extracted with n-hexane prior to analysis. A 3.0-mL aliquot of the solution was collected and filtered through an ultra-four centrifuge ultrafilter (nominal pore size of 1–2 nm) to remove particles within half an hour of centrifugation [35]. The samples were characterized by plasma-mass spectrometry and dynamic light scattering (DLS) for further verification of the undissolved particles in the filtrate. TOC analyzer was used to measure total organic carbon and all the samples were treated with scavenging agent (0.1 M KI) to obtain an accurate value of TOC [36]. All the experiments were conducted in duplicate and average values reported. The error bars are added to all figures that are representing the average error between the experimental values as all the tests were conducted in duplicate.

2.4 Analytical methods

The samples for TCE analysis (1.0 mL) were collected at desired time intervals and extracted with n-hexane (1.0 mL) and then vigorously stirred for at least 3.0 min with a vortex stirrer. The extracts of the samples were maintained quiescent for 5.0 min prior to analysis by gas chromatography (Agilent GC 7890A, Palo Alto, CA, USA). The detector (ECD), oven and injector temperatures were maintained at 260°C , 75°C and 240°C , respectively. High performance liquid chromatography (Varian Prostar 310), equipped with a column ($4.6 \times 150 \times 0.005$ mm), mobile phase of methanol-deionized water mixture (55/45, v/v) and UV detector operated at 237 nm was used for the probe degradation [35]. The samples were immediately quenched with scavenging agent potassium iodide (0.1 M) to acquire accurate TOC values by using a multi 3100 TOC-TN analyzer. The use of the potassium iodide (scavenging agent) possibly leads towards complete reduction of SPC (H_2O_2) and the discharge of the metallic ions. The potassium iodide behaves as a reduction and precipitation agent [26, 36–37]. Electron spin resonance (ESR) spectroscopy was used to determine the presence of $\text{OH}^\bullet$ in solution. The samples (1.0 mL) were collected and quenched with DMPO (1.0 mL, 8.84 mM) for sixty seconds to form DMPO- $\text{OH}^\bullet$ adduct for the elucidation of the hydroxyl radicals. The samples were analyzed using a EMX/8/2.7C, Bruker, Germany with Microwave Bridge (conversion time, 40.96 ms, microwave frequency 9.866 GHz, microwave power 2.016 mW, field sweep 100 G, modulation amplitude 1 G, number of scans 1 and time constant 163.84 ms). The solution pH was measured using pH meter (Mettler Toledo DELTA 320, Greifensee, Switzerland). The leaching of iron and nickel was measured by using inductively coupled plasma-mass spectrometer (ICP-MS, Agilent 7500ce, Agilent Technologies, CA).

3. Results and discussions

3.1 Physico-chemical properties and morphology of zeolite supported iron-nickel bimetallic nano-composite

The morphology and structure of the zeolite and Z-nZVI-Ni bimetallic composite with 5% wt of nickel loading are obtained using SEM and TEM images as shown in Fig. 1(a and b). The smooth surfaces of the zeolite are evident in Fig. 1a. Iron and nickel NPs are highly distributed on the zeolite sheet, producing a hexagonal stippled pattern over a large domain. Measurement of the particle size distribution of the Z-nZVI-Ni composite indicated that most of the particles fall in the range of 1.5–3.0 nm when viewed along the [1 1 0] direction whereas, 3.0–7.0 nm particles were observed occasionally in the Z-nZVI-Ni composite when viewed along the [0 0 1] direction. The SEM and TEM images of other prepared catalysts are shown in Fig. S1. The TEM image of the reused Z-nZVI-Ni showed highly distribution of the iron and nickel NPs on the natural zeolite sheet with almost no signs of aggregation as shown in Fig. S2.

The elemental analysis was performed by using energy dispersive X-ray (EDX) for zeolite and Z-nZVI-Ni as shown in Fig. 1c and d. It is evident that significant amount of iron was present along with nickel in the Z-nZVI-Ni composite. The nickel and iron have mass ratio of 0.044 which is close to the theoretical ratio of 0.052.

The textural properties of the Z-nZVI-Ni composite, other prepared catalysts and reused Z-nZVI-Ni composite were investigated using N₂-adsorption-desorption isotherms as shown in Table S1. It is observed that filling of nitrogen occurred approximately at P/Po = 0.57–0.98 corresponding to the capillary condensation and representing a high degree of uniformity of the pore size of particles. A narrow pore size distribution is confirmed by calculating pore size distribution curves from desorption branches. The BET surface area of the zeolite particles is 0.601 m²/g. However, incorporation of iron and nickel particles on the zeolite sheet significantly increased the BET surface area to 120 m²/g. The average pore size of the Z-nZVI-Ni composite is 7.8 nm, compared to 9970 nm for non-treated zeolite. The above phenomena confirmed that incorporation of iron and nickel significantly increased the BET surface area and pore size of the zeolite. The textural properties of the reused Z-nZVI-Ni also displayed a significant extension in the life of Z-nZVI-Ni for further usage. The possible reason behind this may be the inhibition of shrinkage of the aluminosilicates matrix due to the high distribution of iron and nickel NPs in its matrix.

The powder wide angle X-ray diffraction (WA-XRD) profile of iron and nickel deposited on the zeolite sheet is shown in Fig. 2a. The WA-XRD profile clearly indicates the presence of the face centered cubic nickel (fcc-Ni) (JCPDS card # 01-1260) with diffraction peaks at 44.8°, 52.9° and 69.8° respectively. The diffraction peaks at 42.7° and 62.2° are associated with iron particles, whereas the peaks at 28.9° and 35.4° show the existence of lepidocrocite and maghemite (γ -Fe₂O₃) (JCPDS card # 89-5892). It is also observed that most of the aluminosilicate peaks present in the zeolite disappeared with new diffraction peaks of iron, fcc-Ni and lepidocrocite and maghemite (γ -Fe₂O₃) with positive shift. The Scherrer equation was used to determine the size of the particles [38–39].

The estimated average particle size of the Z-nZVI-Ni using above equation is 4.9 nm, which is consistent to that of the TEM results. The WA-XRD of the reused Z-nZVI-Ni also showed no significant changes even after first run of the Z-nZVI-Ni as shown in Fig. S4.

The FTIR-spectra analysis of zeolite and Z-nZVI-Ni with wave number of 280–4000 cm^{-1} was performed as shown in Fig. 2b. The absorption spectral peaks of the zeolite near 465, 685 and 1105 cm^{-1} are attributed to the internal vibrations of the bending, rocking and stretching of the Al-O-Si bridge. The group bands other than mentioned above are associated with the external and lattice vibrations. The presence of the double four rings (D4R) is suggested near the spectral band of 565 cm^{-1} that is significantly present in the zeolite [40]. In addition, cations are assigned to the spectral peaks in the range of 1200–1600 cm^{-1} . However, a significant change in the structure of the Z-nZVI-Ni is observed with appearance of new characteristic peaks with a relatively low intensity than the zeolite. The characteristic peaks of the nickel oxides is believed to be below 1000 cm^{-1} . The spectral peak near 440 cm^{-1} is Ni-O [39] bonding on the Al-O-Si bridge showing the presence of nickel in Z-nZVI-Ni composite. The iron NPs appeared at a spectral peak near 535 cm^{-1} [41]. The H-OH bending vibrations appeared near the characteristic peaks heights of 3435 and 1635 [39]. The appearance of new characteristics spectral peaks of iron and nickel with changed intensities on the framework of the zeolite showed that these results are consistent with the XRD results.

3.2 Degradation of trichloroethene in Z-nZVI-Ni-percarbonate system

The catalytic activity of the prepared Z-nZVI-Ni was investigated for the degradation of TCE, with the results compared to those of control experiments conducted in the absence of SPC and catalyst. The removal of TCE due to adsorption was measured before the evaluation of TCE degradation. All the reagents were stirred vigorously for one hour to achieve the adsorption-desorption equilibria between TCE and the Z-nZVI-Ni without the addition of SPC as shown in Fig. S5 since the equilibria was confirmed in one hour because no significant difference was found in the next hour as depicted in the Fig. S6. For the purpose of comparison, the catalytic activity of the prepared Z-nZVI-Ni was also compared to the other catalysts including Z-nZVI-Cu, Z-nZVI, nZVI, nZV-Ni and zeolite.

It is observed that the adsorption of TCE by Z-nZVI-Ni increased from 18.7% to 27.8% as the nickel contents in the Z-nZVI-Ni increased from 1% to 5% by weight, but further increase in nickel content (10%) did not show any significant further increase in adsorption (28.9%). However, all other prepared catalysts i.e. Z-nZVI-Cu (21.4%), Z-nZVI (15.8%), nZVI (7.5%), nZV-Ni (11.5%) and zeolite (3.2%) showed decreased adsorption of TCE as compared to Z-nZVI-Ni. This higher adsorption characteristic of Z-nZVI-Ni is associated with its higher surface area (120 m^2/g) and higher pore size (7.8 nm) [24].

The catalytic ability of Z-nZVI-Ni compared with other catalysts is shown in Fig. 3a. The TCE degradation rates achieved are 47%, 69% and 70% by using 1.0, 5.0, and 10% (wt %) nickel loading on Z-nZVI-Ni composite under the same experimental conditions. Whereas, TCE degradation rates are 56%, 40%, 27%, 22%, 2.9% and 3.7% for Z-nZVI-Cu, Z-nZVI, nZVI, nZV-Ni, only SPC, and only zeolite respectively. The Z-nZVI-Ni (5%) was used as a catalyst for the rest of the experiments because of no significant difference of adsorption

ability and degradation efficiency found between Z-nZVI-Ni (5%) and Z-nZVI-Ni (10%). No significant increase in performance of Z-nZVI-Ni (10%) might be due to the higher nickel contents increased the surface area of the nickel and decreased the exposure of iron particles to the solution. The nickel alone could degrade TCE but in the case of combined iron and nickel as a catalyst, nickel behaves as catalyst instead of reducing agent whereas, iron due to its low reduction potential behaves as a reducing agent as previously reported [42–43].

The TCE degradation rates were 95%, 63%, 48%, 21% and 2.5% catalyzed by Z-nZVI-Cu, Z-nZVI, nZVI, nZV-Ni, and SPC only, respectively, for an increased catalyst dosage of 250 mg/L (Fig. 3b). Minimal degradation of TCE is observed when only SPC was used for the degradation of TCE, demonstrating its weak oxidation potential as compared to hydroxyl radicals. However, almost complete degradation of TCE is achieved when catalyzed by Z-nZVI-Ni, indicating its exceptional catalytic capability for the activation of SPC. This enhanced TCE degradation is due to the enhanced physico-chemical properties of the Z-nZVI-Ni and combined effect of iron and nickel particles highly dispersed on the zeolite sheet, producing large reactive surface area for the enhanced and efficient catalytic capability of the Z-nZVI-Ni composite for the activation of SPC. Similar types of catalysts have been reported showing enhanced catalytic ability due to the use of the supporting materials. For instance, Wu showed the catalytic activity of iron and nickel NPs supported on cellulose acetate for the removal of trichloroethylene [20]. Kong demonstrated the enhanced catalytic capability of manganese monoxide supported on mesoporous carbon for the complete mineralization of phenol [44]. In short, the support material has a very important role in the degradation of the organic contaminants like TCE as the reactions occur on the active sites of the surface leading towards the decreased mass transfer resistance between reactants and products, which ultimately improves the performance.

The reaction kinetics of TCE degradation was investigated by using pseudo first order kinetic model. This kinetics can be expressed as Eq. 6

$$-\ln (C_i/C_o)=k t \quad (6)$$

Where C_i and C_o are the concentrations of TCE at time (t) and at initial and k is the apparent rate constant that was calculated from the slope of the line by plotting $-\ln (C_i/C_o)$ versus time (t). The regression lines were achieved by plotting $-\ln (C_i/C_o)$ against t (min) along with correlation coefficients (R^2) of 0.99, 0.98, 0.97 and 0.95 respectively as shown in Fig. 4. The above kinetic analysis demonstrated that TCE degradation follows pseudo first order kinetic behavior. The apparent reaction rate constant of Z-nZVI-Ni was 2.2 hr^{-1} , much higher than rate constants of 1.0 hr^{-1} (Z-nZVI-Cu), 0.27 hr^{-1} (Z-nZVI) and 0.20 hr^{-1} (nZVI) respectively. It is observed that the TCE degradation rate constant for Z-nZVI-Ni is 11 folds greater than nZVI, 8 folds greater than Z-nZVI and more than 2 folds greater than Z-nZVI-Cu respectively. TCE degradation rate was strongly linked to the initial concentration of TCE and the active surface sites of catalyst, i.e. Z-nZVI-Ni. The elucidation of the higher rate constant of Z-nZVI-Ni is associated with its significant higher catalytic

ability than the other prepared catalysts. Addition of Ni may be an additive advantage in increasing the rate constant of Z-nZVI-Ni as compared to other catalysts as the experimental conditions were same in preparing all catalyst composites. A study conducted by Wang also demonstrated that addition of second metal on the mesoporous carbon support produced an enhanced effect due to which rate constant increased four folds and the degradation of bisphenol A occurred at a faster rate [24].

Various catalyst dosages and SPC concentrations were applied to investigate their effects on TCE degradation. Different experimental conditions were also evaluated for the degradation of TCE with respect to reaction time. It is observed from Fig. 5 that there is no significant effect on TCE degradation when catalyst dosage increased from 100 to 150 and then 200 mg/L. For example, 69%, 71%, and 76% of TCE were degraded using 100 to 150 and 200 mg/L of Z-nZVI-Ni whereas, further increase in catalyst dosage to 250 and 300 mg/L completely degraded TCE in the same interval of time. Therefore, 250 mg/L of Z-nZVI-Ni was used as an ideal loading in all other experiments due to the low quantity of catalyst usage and cost of the catalyst. A maximum rate constant (2.2 hr^{-1}) was achieved with 250 mg/L loading of Z-nZVI-Ni confirming its heterogeneous behavior along with R^2 value of 0.99. This increased amount of Z-nZVI-Ni increased the availability of the more active sites available for reactions leading towards the complete destruction of TCE.

The effect of various concentrations of SPC on the catalytic ability of Z-nZVI-Ni was also elucidated. The stoichiometric equation showing the reaction between TCE and SPC is Eq. 7 [2].

According to the above equation, 0.3 mM of SPC can mineralize 0.15 mM of TCE theoretically. Fig. 6 shows the TCE degradation efficiencies in 1.0, 50, 10 and 15 mM concentrations of SPC. The TCE degradation was significantly enhanced from 42% to 70% and 99.8% when SPC concentration increased from 1.0 to 5.0 mM and 10 mM. However, further increase in SPC to 15 mM suppressed the TCE degradation, which might be due to the consumption of SPC from the scavenging characteristic of SPC as shown in the following equations [9–11]. Miao also demonstrated in Fenton like process that the higher concentrations of SPC (H_2O_2) followed quenching reactions which leads towards consumption of $\text{OH}^\bullet$ i.e. Eqs. 8–10 [10–12].

3.3 Potential reaction mechanism

The 5,5-dimethylpyrroline-1-oxide (DMPO) spin trap electron spin resonance (ESR) was used to investigate $\text{OH}^\bullet$ generation in the heterogeneous Fenton like reaction to fully understand the reaction mechanism [11]. The signals of DMPO- $\text{OH}^\bullet$ adduct achieved by Z-nZVI-Ni as a catalyst for the SPC activation are shown in Fig. 7. It is observed that Z-nZVI-Ni exhibited a four-fold characteristic peaks of DMPO- $\text{OH}^\bullet$ adduct with a stronger intensity of ratio of 1-2-2-1. This is a clear indication that Z-nZVI-Ni can efficiently activate SPC for $\text{OH}^\bullet$ generation in the system demonstrating its enhanced catalytic reactivity. For the purpose of comparison, ESR spectra of the Z-nZVI-Cu, Z-nZVI, nZVI and zeolite sheet were also measured as shown in Fig. S3. The results indicate less intensity of signals of DMPO- $\text{OH}^\bullet$ adduct as compared to Z-nZVI-Ni. It is also observed that zeolite sheet did not show any signals of DMPO- $\text{OH}^\bullet$ adduct, demonstrating its negligible role for the activation of SPC.

To further confirm the quantification of the $\text{OH}^\bullet$ radicals in our system, *p*-chlorobenzoic acid (500 μM) was used as a probe compound [35]. It is observed that 96% of *p*-chlorobenzoic acid was degraded when Z-nZVI-Ni was used as a heterogeneous catalyst (Fig. 8a). Whereas, the degradation of *p*-chlorobenzoic acid achieved by using Z-nZVI-Cu, Z-nZVI and unsupported-nZVI were 91%, 55% and 44% respectively. This confirms its exceptional catalytic reactivity to produce $\text{OH}^\bullet$ radicals in our system. It can be suggested from Fig. 8a that the degradation of *p*-chlorobenzoic acid by using other catalysts showed less catalytic reactivity than Z-nZVI-Ni. The *p*-chlorobenzoic acid degradation trend obtained by Z-nZVI-Ni is also consistent with the trend of TCE degradation. The first reason behind the increased generation of $\text{OH}^\bullet$ radicals might be the exposure and the presence of more active sites available on the surface of Z-nZVI-Ni due to the enhanced surface area and reduced particle size [45]. The second reason might be the combined effect of nickel and iron thoroughly distributed on the zeolite sheet which can also contribute in the stability of the Z-nZVI-Ni. The average molar concentration of the $\text{OH}^\bullet$ radicals can be derived from the *p*-chlorobenzoic acid curve by

$$C = \int_0^T (C_i - C_o) dt / T \quad (11)$$

Here, *C* is the average molar concentration of $\text{OH}^\bullet$ radicals, *C_o* and *C_i* are the initial and final molar concentrations of the *p*-chlorobenzoic acid after a time of *t* (h) and *T* is the total exposure time of 3 h. The $\text{OH}^\bullet$ radicals generated by Z-nZVI-Ni were 480 μM , significantly higher than other prepared catalysts as shown in Fig. 8b. The apparent rate constant of the Z-nZVI-Ni for the degradation of *p*-chlorobenzoic acid was 1.032 hr^{-1} that was 1.2, 4.7 and 6.6 folds greater than the rate constants of the Z-nZVI-Cu, Z-nZVI and nZVI respectively. Based on the above results, it was concluded that $\text{OH}^\bullet$ radicals are playing dominant role as an oxidizing reactive species in the Z-nZVI-Ni system. In addition, nickel may contribute in

the stability of iron itself. The low removal efficiency obtained using Z-nZVI can be attributed to the fact that the corrosion of Z-nZVI led to a rapid formation of surface-passivating oxide layers. These oxide layers blocked the active sites on the surface of Z-nZVI and hence inhibited direct electron transfer from the iron surface to TCE.

A potential reaction mechanism is suggested on the basis of XRD, ESR spectra obtained and degradation of *p*-chlorobenzoic acid by using Z-nZVI-Ni as a heterogeneous catalyst. The heterogeneous Fenton like reaction catalyzed by Z-nZVI-Ni involves surface reactions with the combined participation of iron and nickel active sites. The iron (Fe^0) present in the Z-nZVI-Ni transforms to Fe^{2+} via two electron transfer from nanoparticle surface to SPC (H_2O_2) as described in the Eqs. 12–13 [16, 46]. This Fe^{2+} accelerates the H_2O_2 to generate $\text{OH}^\bullet$ radicals via Haber–Weiss mechanism as described in the Eq. 14. The simultaneous transformation of Fe^{2+} to Fe^{3+} can be proceeded through Eqs. 15–16. In a similar way, Ni^+ may also contribute in the activation of SPC for the $\text{OH}^\bullet$ radical generation. The subsequent reactions may proceed as Eqs. 17–19.

The standard reduction potential of $\text{Fe}^{3+}/\text{Fe}^{2+}$ is 0.77 V whereas, $\text{Ni}^{+2}/\text{Ni}^{+}$ is -0.25 V which confirms the thermodynamically favorable situation for the reduction of Fe^{3+} by Ni^{+} . Z-nZVI-Ni bimetallic nanoparticles generated high surface area and density of surface active sites which is attributed to its excellent performance for the removal of contaminants [28]. Hence, the interfacial electron transfer is increased significantly in Z-nZVI-Ni, showing the combined effects of iron and nickel on the zeolite sheet by increasing its catalytic reactivity for TCE degradation. The existence of intermediate and final products was elucidated by using GC-MS. The results confirmed the presence of dichloroacetic acid, vinyl chloride, and oxalic acid as intermediate products, further transformed to water, chloride ions, and carbon dioxide as end products as shown in Fig. 9. The key role of Z-nZVI-Ni has been elucidated in producing environmentally friendly end products that might be due to higher catalytic reactivity, stability and interfacial electron transfer of Z-nZVI-Ni.

3.4 Total organic carbon removal and dechlorination of TCE

Total organic carbon (TOC) removal was measured to investigate the mineralization of TCE in SPC system catalyzed by the various catalysts by using TOC analyzer. It is observed from Fig. 10a that the removal of TOC was 89.6% when Z-nZVI-Ni was used as a catalyst for the activation of SPC corresponding to the almost complete TCE degradation, exhibiting a high catalytic reactivity of Z-nZVI-Ni to mineralize TCE. Conversely, less TOC removal is observed with the same comparable amounts of other catalysts for the activation of SPC. For example, 75.2, 59.2, 41, 2.4 and 16.5% TOC removal efficiencies were found in the cases of Z-nZVI-Cu, Z-nZVI, nZVI, only SPC and nZV-Ni, respectively, corresponding to 95, 63.7, 48, 2.5 and 21.8% TCE degradation efficiencies. It was expected that there would have change in physico-chemical properties of the Z-nZVI-Ni by oxidation due to the transformation of metallic iron and nickel to their corresponding cations. So, TOC removal performance was also determined using reused Z-nZVI-Ni (second run) as shown in the Fig. 10b. TOC removal was significantly higher in the case of Z-nZVI-Ni (78.3%) still after second run whereas, more decrease in TOC removal was observed in the case of other comparative catalysts. For instance, TOC removal was 60.8%, 39.9%, 24.5%, 0.9% and 7.8% by using Z-nZVI-Cu, Z-nZVI, nZVI, only SPC and nZV-Ni respectively. These results demonstrated that the reused Z-nZVI-Ni has extended catalytic ability for effective TOC removal yet. Furthermore, the effect of different Z-nZVI-Ni loadings for TOC removal was also elucidated. The Z-nZVI-Ni loadings were 100, 150, 200, 250 and 300 mg/L as shown in the Fig. S7. No significant effect on TOC removal was observed initially when the catalyst dosages increased from 100 to 200 mg/L. Like TCE degradation, TOC removal was sufficiently increased when catalyst dosage reached 250 mg/L, whereas, further increase in catalyst dosage did not produce profound effect on TOC removal.

In order to investigate the efficiency of Z-nZVI-Ni for the liberation of chlorine ions (Cl^{-}), TCE dechlorination efficiency was calculated as shown in Fig. 11. The chloride ions released were 0.123 mM corresponding to the TCE dechlorination rate of 82.5%, to some extent less than TOC removal efficiency of 89.6% when Z-nZVI-Ni was used as a catalyst. However, chloride ions liberated by Z-nZVI-Cu, Z-nZVI, nZVI and nZV-Ni are 0.097, 0.07, 0.048 and 0.022 mM against the 65.2, 46.7, 32.6 and 15.3% dechlorination efficiencies,

somehow lower than TOC removal efficiencies of 75.2, 59.2, 41 and 16.5% respectively. These results further confirmed the higher activity of the Z-nZVI-Ni over other catalysts.

3.5 Leaching and reusability of Z-nZVI-Ni

The leaching of iron and nickel in the solution is an important parameter that can predict the stability of the catalyst in the long term applications. The change in the catalytic activity of the Z-nZVI-Ni and leaching was studied with respect to the actual applications. The concentrations of total dissolved iron and nickel were 0.25 mg/L and 0.02 mg/L without SPC whereas, in the presence of SPC, 0.47 mg/L and 0.03 mg/L respectively by using ICP-MS instrument. The slow leaching of iron and nickel validated the higher stability of the Z-nZVI-Ni that may be because of the strong interactive force present between iron and nickel on the natural zeolite sheet. Moreover, to further re-confirm the stability characteristics, the reusability of the Z-nZVI-Ni was elucidated for the degradation of TCE in various set of experiments as shown in Fig. 10c. The catalytic activity of the Z-nZVI-Ni for the degradation of TCE in five consecutive runs were 99.9%, 94.9%, 89.6%, 70% and 59% respectively. These results further confirmed that the addition of nickel was a valuable addition with nano zero valent iron on the framework of natural zeolite in extending the life of the Z-nZVI-Ni significantly.

Conclusion

Natural zeolite supported iron-nickel bimetallic ultra-fine nanoparticles composite (Z-nZVI-Ni) has been demonstrated as a heterogeneous catalyst in the present study. The results showed that the incorporation of iron and nickel particles on the zeolite sheet significantly increased the BET surface area to 120 m²/g. The adsorption of TCE by Z-nZVI-Ni increased from 18.7% to 27.8% as the nickel contents in the Z-nZVI-Ni increased from 1% to 5% by weight with complete TCE degradation. However, further increase in nickel content (10%) did not show any significant increase in adsorption (28.9%). The TOC removal and mineralization of TCE by using the Z-nZVI-Ni with a dosage of 300 mg/L and SPC (10 mM) was maximized as compared to other prepared catalysts at identical experimental conditions. The major benefit of Z-nZVI-Ni composite is its increased surface area that significantly favored the rapid reaction of reactants. Another benefit of Z-nZVI-Ni is the increment in the active sites due to high dispersion of iron-nickel bimetallic NPs on the natural zeolite sheet. Additionally, the combined effect of iron-nickel bimetallic NPs enabled the reduction and oxidation of Fe³⁺ to Fe²⁺ and Ni²⁺ to Ni⁺ to enhance the catalytic efficiency of Z-nZVI-Ni. In conclusion, the SPC system catalyzed by Z-nZVI-Ni as a heterogeneous catalyst offers a promising technique for the remediation of TCE contaminated groundwater.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Fig. 1. The characteristics of morphologies and energy dispersive X-ray (EDX) analyses of (a) zeolite using SEM, (b) Z-nZVI-Ni using TEM, (c) zeolite using EDX, (d) Z-nZVI-Ni using EDX.

Fig. 2.
 (a) Wide angle X-ray diffraction (WA-XRD) patterns of Z-nZVI-Ni, (b) Fourier transform infrared spectroscopy (FTIR) differential spectrum of zeolite and Z-nZVI-Ni.

Fig. 3.

The degradation of TCE using SPC catalyzed by Z-nZVI-Ni, Z-nZVI-Cu, Z-nZVI, nZVI, nZV-Ni, and SPC alone, (a) ($[TCE]_0 = 0.15$ mM, $[SPC] = 10$ mM), $[catalyst] = 100$ mg/L, (b) ($[TCE]_0 = 0.12$ mM, 0.13 mM, 0.14 mM, 0.13 mM, 0.15 mM, 0.15 mM, $[catalyst] = 250$ mg/L, $[SPC] = 10$ mM).

Fig. 4.
The kinetic analysis of TCE degradation with the different catalysts.

Fig. 5.

The degradation of TCE in a percarbonate catalyzed system with various Z-nZVI-Ni catalyst dosages ($[TCE]_0 = 0.15$ mM, $[SPC] = 10$ mM).

Fig. 6.

The degradation of TCE in a percarbonate catalyzed system by Z-nZVI-Ni under various SPC dosages ($[TCE]_0 = 0.15$ mM, $[catalyst] = 250$ mg/L).

Fig. 7. The electron paramagnetic resonance (EPR) spectra of hydroxyl radicals by Z-nZVI-Ni using DMPO spin-trapping (samples taken at 60 second).

Fig. 8.

The $\text{OH}^\bullet$ generation kinetics indicated by (a) degradation of p-chlorobenzoic acid ($500 \mu\text{M}$) by Z-nZVI-Ni, Z-nZVI-Cu, Z-nZVI and nZVI catalyzed percarbonate system, (b) quantitative measurement of hydroxyl radicals, Z-nZVI-Ni = Z-nZVI-Cu = Z-nZVI = nZVI = 250 mg/L , SPC = 10 mM .

Fig. 9.

A possible pathway of TCE degradation due to reactive oxygen species ($\text{OH}^\bullet$) in the Z-nZVI-Ni catalyzed percarbonate system.

Fig. 10. TOC removal in the presence of various catalysts in the (a) first run, (b) second run (reused). Z-nZVI-Ni = Z-nZVI-Cu = Z-nZVI = nZVI = nZV-Ni = SPC only = 250 mg/L, (c) the reusability of the Z-nZVI-Ni in various experimental runs.

Fig. 11.

TCE dechlorination in the presence of various catalysts. Z-nZVI-Ni = Z-nZVI-Cu = Z-nZVI = nZVI = nZV-Ni = SPC only = 250 mg/L.