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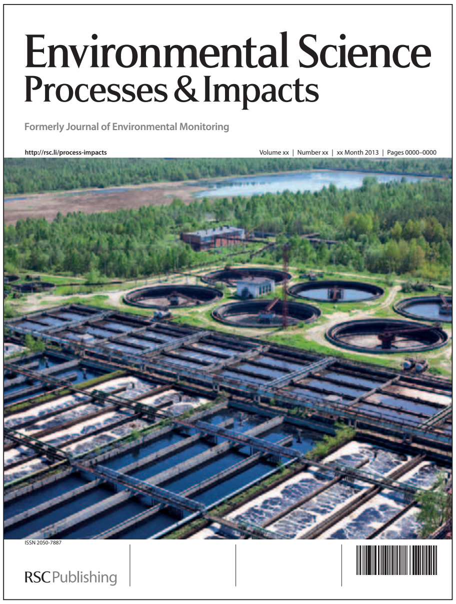

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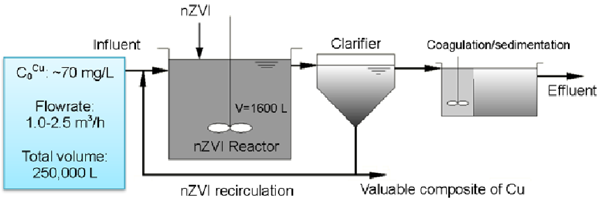

Environmental impact statement

This work is the first field application of zero-valent iron nanoparticles (nZVI) for industrial wastewater treatment. We demonstrated a green process to treat wastewater and recover heavy metal. A field pilot test was conducted using 55 kg nZVI to treat a total of 250,000 L wastewater containing high level of Cu(II). The pilot test was operated continuously. To make the process affordable, nZVI was re-circulated and reused. The nZVI process presented is designed for large-scale applications and easy-to-maneuver. Results suggest that this nZVI process is much more efficient than conventional technologies of wastewater treatment, and copper could be easily recovered from wastewater using this process.

Nanoscale Zero-Valent Iron (nZVI) for Treatment of Concentrated Cu(II) Wastewater: A Field Demonstration

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Abstract

Field demonstration was conducted to assess feasibility of nanoscale zero-valent iron (nZVI) for treatment of wastewater containing high levels of Cu(II). Pilot tests were performed at a printed-circuit-board manufacturing plant, treating 250,000 L of wastewater containing 70 mg/L Cu(II) with a total of 55 kg of nZVI. A completely mixed reactor of 1,600 L was operated continuously with flow rates ranging from 1,000 to 2,500 L/h. Average Cu(II) removal efficiency was greater than 96% with 0.20 g-nZVI/L and a hydraulic retention time of 100 min. The nZVI reactor achieved a remarkably high volumetric loading rate of 1,876 g-Cu/m^3•d for the Cu(II) removal, surpassing the loading rates of conventional technologies by more than one order of magnitude. Average removal capacity of nZVI for Cu(II) was 0.343 g-Cu/g-Fe. The Cu(II) removal efficiency can be reliably regulated by the solution E_h, which in turn is a function of nZVI input and hydraulic retention time. Ease of separation and recycling of nZVI contribute to process up-scalability and cost effectiveness. Cu(II) was reduced to metallic copper and cuprite (Cu_2O). The end product is a valuable composite of iron and copper (~20-25%), which can partially offset the treatment costs.

Introduction

Due to the wide applications of copper in industrial and household products, cupric ion (Cu(II)) is commonly found in industrial effluents, such as copper smelting, electroplating, and manufacturing of electronic devices including printed circuit boards (PCB). In China, it was estimated that these industries produce more than 1 billion cubic meters of wastewater per year, according to an annual report from National Bureau of Statistics of China. Industrial effluents are the main anthropogenic sources of copper released into the environment.[1]

This study aims to prove an efficient and operationally facile method for decontaminating industrial waste streams. Conventional methods of wastewater treatment for Cu(II) removal include chemical precipitation, adsorption, ion exchange etc. Among them, chemical precipitation by lime or sulfide salts (e.g., Na_2S) has been widely applied because of the low costs.[2,3] Due to the Cu(II) solubility limitation, excessive amounts of chemicals are often required to meet stringent discharge standards,[3] and these processes often generates large quantities of sludge. Disposal of those hazardous solid wastes demands additional costs and brings up safety concerns. Applications of ion exchange resins and adsorbents in industrial streams are limited due to high capital and maintenance costs. Removal capacities of most adsorbents are low, typically at the level of a few grams per kilogram.[4]

Application of zero-valent iron (ZVI) for heavy metal removal has attracted interests of many researchers and industrial practitioners, owing to its low cost and an environmental benign character.[5-8] Nevertheless, since its first reported application in early 1990s, ZVI technologies have been largely used for remediation of contaminated groundwater. Limited information is available on its practice in industrial wastewater. Treating industrial streams presents unique challenges, as they often contain high levels of contaminants in the presence of a complex mixture of various chemicals and impurities. ZVI technologies tailored for groundwater may fall short of the requirements for effective industrial wastewater treatment. For example, low-reactivity bulk ZVI materials were often used in ZVI-based permeable reactive barriers (Fe-PRBs) for groundwater remediation. Elevated concentrations of pollutants in the inflow often resulted in fast breakthrough of the barriers or required prolonged contact time. Suspended solids, anions and organic substances in industrial streams are known to cause permeability loss and ZVI surface fouling, rendering gradual effluent quality deterioration with operational time.[9-11] To cope with industrial effluents, high-efficiency and easy-to-operate ZVI technology are often desired.

Recently, nanoscale zero-valent iron (nZVI) is gaining popularity due to its enhanced reactivity compared to conventional bulk ZVI materials.[12] The enhancement effect is attributed to the large surface-to-volume ratio provided by the diminutive size. Outstanding performance of nZVI for Cu(II) removal has been reported in a number of lab studies[13-16]. However, these studies were typically conducted in small batch reactors using synthesized Cu(II) solutions. Large-scale application of nZVI in real industrial wastewater has yet not been reported.

Compared to the batch-mode lab experiments, wastewater facilities are mostly operated with continuous flow reactors, particularly, continuous flow stirring tank reactor (CFSTR). CFSTRs possess the advantage of a high buffering capacity against fluctuations in the influent characteristics. So far, no study has reported the use of nZVI in these reactors.

The nanoscale size of nZVI provides favorable hydraulic characteristics for its use in CFSTR (e.g., mixing and pumping). The gravity of nZVI can easily be conquered by the sheer force arising from turbulent flow generated by continuous mixing. High velocity gradient introduced by mixing also enhances the mass transfer and at the same time reduces the formation of coating on iron surfaces that may lead to surface passivation.

In this work, we report the first application of nZVI in industrial wastewater treatment and study on the performance parameters of a CFSTR-based treatment system. A 1600-L CFSTR reactor was fed with nZVI and operated continuously to treat Cu(II)-containing wastewater at flow rates of 1.0-2.5 m^3/h. nZVI suspension in this CFSTR was sustained by continuous stirring and a nZVI recovery unit was incorporated after the CFSTR to recycle the nZVI. The objective was to evaluate the efficiency and also cost of nZVI as a viable means to treat industrial streams with high metal content. It is expected that results from this study can fill in the gaps between lab studies and implementations in industrially relevant reactor systems. The pilot results also generate knowledge to guide the future design and process scale-up of nZVI technology for industrial water treatment.

Materials and methods

Batch experiments

Fresh nZVI was prepared by the reduction of ferric ions with sodium borohydride.[17] Specific surface area (SSA) of nZVI was 30 m^2/g based on N_2-BET measurement. For batch tests, Cu(II) solutions were prepared using copper chloride ($CuCl_2$•$2H_2O$, Aladdin, Shanghai) and deionized water. Batch tests were performed using 1000 mL nZVI slurry

(2.0 g/L nZVI) at 22°C in a 7-neck flask equipped with a mechanical rotating paddle. The solutions were purged with high-purity nitrogen gas continuously throughout experiments. pH and oxidation-reduction potential (ORP) electrodes were fitted into the flask to monitor changes in solution pH and E_h during the experiments. After E_h of the nZVI slurry became stable, the flask was spiked sequentially with 32 ml of a Cu(II) stock solution (12 g-Cu(II)/L). One sample (16 ml) was withdrawn five seconds after spike, and the second one (16 ml) was taken before re-spiking. All samples were filtered with 0.2-μm PTFE syringe filters. Dissolved copper concentrations were determined using an inductively coupled plasma spectrometer (ICP, Agilent 720ES). Removal capacity of nZVI was evaluated based on the total amount of Cu(II) removed.

Pilot experiment

Influent of the pilot experiment was pumped from the equalization basin of a wastewater treatment facility in a printed circuit board (PCB) factory. The pilot plant and treatment process are illustrated in Figure 1 (a-d). The pilot plant consisted of three tanks, including a nZVI reactor, a clarifier, and an integrated coagulation-sedimentation tank, plus additional accessories such as a feeding pump and a sludge recirculation pump. The square-shaped reactors were made of white polyvinyl chloride (PVC) and reinforced with stainless angle steel frames (Figure 1b). The nZVI reactor was 1600 L in volume and agitated by a mixing blade powered with a 1.5-kW electrical motor. A peristaltic pump was used to feed the reactor with nZVI stock slurry. pH and ORP of the nZVI suspension in the reactor were monitored by online pH and ORP electrodes. ORP values were corrected with respect to Ag/AgCl reference electrode and converted to values against the standard hydrogen electrode potential (E_h). The clarifier after nZVI reactor served to separate nZVI particles from the bulk solution. The settled nZVI was recycled to the nZVI reactor by a pump. Effluent from the clarifier was further treated by a conventional coagulation/flocculation process to remove remaining solids. Poly-ferric sulfate (PFS) was used as a coagulant and polyacrylamide (PAM) as a coagulant aid. The pilot system operated continuously during each individual test, and at the completion of a test, it was evacuated and restarted for the next test.

Solid characterizations

Residual solids recovered from batch flasks and the pilot reactors were dried in a glove box under N_2 atmosphere, and analyzed using an X-ray diffractometer (XRD, D8-advanced). Surface morphology and elemental composition of nZVI particles were analyzed with a Hitachi S-4300 field emission scanning electron microscope with energy-dispersive X-ray spectroscopy (SEM-EDS).

Results and discussion

Pilot operations

Pilot tests were conducted at five flow rates, 1.0, 1.25, 1.5, 2.0, and 2.5 m^3/h. 250 m^3 of PCB wastewater was treated using a total of 55 Kg nZVI. Photos of pilot facilities and flow chart are presented in Figure 1. Operational parameters and Cu removal performance were summarized in Table 1 and Figure 2 respectively. Figure 2a presented Cu(II) concentrations in the influent and effluent throughout the pilot tests, and Figure 2b delineated the accumulative amounts of nZVI and Cu(II) in the reactor. nZVI used and Cu(II) retained by the reactor by the end of each test were also listed in Table 1.

High removal efficiency (> 96%) was achieved at the hydraulic retention time (HRT) of 1.6 and 1.3 h. Cu(II) concentrations in the effluents were mostly less than 0.5 mg/L at the HRT of 1.6 h, and met the local pretreatment standard (<2 mg/L, Figure 2a), although during the same period the influent experienced intense fluctuations. 97% of Cu(II) (a total of 3.3 kg) in the solution was removed, only a small fraction (~3% or 0.1 kg total) passed through the treatment system (Table1).

Table 2 compared major operational parameters and performance of this CFSTR reactor with those of conventional packed-bed or batch reactors from some published reports. The HRTs of nZVI CFSTR reactor in this study, 1.3 to 1.6 hours, were less than those of packed-bed reactors (7-34 hours) and comparable to those of physico-chemical processes of wastewater treatments. The HRT reduction brings down capital expenses and operation costs, which are among the decisive issues in process selection. The new nZVI setup is more affordable compared to conventional packed-bed configuration.

The treatment performance can be conveniently evaluated by the amount of metals removed per unit volume of reactor. This is often termed the volumetric loading rate, grams of Cu(II) per cubic meter per day (g-Cu/m^3•day). Similar terminology is commonly used in the activated sludge system which is defined as the amount of BOD or COD applied in a unit volume of the aeration tank per day (g-BOD/m^3•d). In this work, the average volumetric loading rate was 1,876 g-Cu/m^3•d at the HRT of 1.6 h, which is 10-200 times higher than those of packed columns using conventional ZVI materials (Table 2). This result suggests that this CFSTR configuration is effective at minimizing the reactor size. The high efficacy of CFSTR might be attributed to several reasons. The reduction of Cu(II) by metallic iron is a surface-mediated reaction of which the reaction rate is proportional to surface area of nZVI.[19,20] The initially formed Cu(0) on the nZVI surface serves as a more efficient cathode material than Fe(0) and as a result it accelerates further Cu(II) reduction. As surface area of nZVI was 10-1000 times greater than those of bulk iron, a much higher reaction rate can be attained with nZVI at an equivalent mass loading.[12] Due to the large electrochemical potential difference (ΔE_h^0 = 0.78 V) between the Fe(II)/Fe and Cu(II)/Cu couples, this reduction reaction has a high intrinsic reaction rate, and thus mass transfer becomes the rate limiting step.[9,16] Mass transfer can be enhanced through vigorous mixing to reduce the thickness of mass transfer boundary layer at the nZVI-water interface. Continuous mechanical mixing also accelerates particle collision and abrasion, thereby reducing the precipitation of iron hydroxides on particles which could impede electron transfer between nZVI and Cu(II). As a comparison, in a ZVI fixed-bed reactor, pore water velocity is typically less than 0.1 mm/s,[5] generating low efficiency in mass transfer and a higher susceptibility to mineral fouling.

Effects of hydraulic retention time (HRT): In order to evaluate the maximum treatment capacity of the reactor, the pilot reactor was further evaluated at higher flow rates (Figure 2a and Table1). Results indicated that, at higher flow rates the effluent became more susceptible to influent fluctuations (Figure 2a), with more Cu(II) escaped from the reactor. For example, at HRT of 0.6 h, only 26% Cu(II) (0.77 Kg) in the influent was captured by the nZVI treatment (Table 1), which was considerably lower than the 96% Cu(II) removal with HRT at 1.6 h.

Effects of input loading: Tests show that the key parameters dictating the performance of this CFSTR are nZVI dose, initial Cu(II) concentration, and the HRT of the nZVI reactor. ZVI kinetics results available from literature were mostly obtained from classic batch reactors,[13,16] and the effects of reaction time, initial Cu(II) concentration, iron concentration were assessed separately. Kinetics results obtained from these studies were unable to provide direct guidance for the scale-up design and process optimization. For example, questions remain in quantifying the effects of each increment in HRT or nZVI dosing on overall removal efficiency.

Therefore, we propose to use a combined parameter incorporating HRT, initial Cu(II) concentration and nZVI concentration, referred herein as the “input loading”, to evaluate the reactor performance.

$$\text{Input loading (L)} = \frac{QC_0}{VC_{Fe}} = \frac{C_0}{HC_{Fe}} \qquad \text{Unit: g-Cu/(g-Fe•h)} \qquad (1)$$

where Q = volumetric flow rate (L/h), V = reactor volume (L), C_0 = influent Cu(II) concentration (g/L), C_{Fe} = nZVI concentration in the reactor (g/L), and H = hydraulic retention time (hour). The input loading here means the mass of Cu(II) applied to per unit mass of nZVI per unit of time, similar to the Food/Microorganism (F/M) ratio which was defined as the rate of BOD or COD applied per unit volume of mixed liquor (g-BOD,COD/g-VSS•h) in activated sludge.

Pilot performance was re-examined on the basis of the input loading calculated using Equation (1). Statistical data were shown due to the fluctuations of the influent (Figure 3). Results indicate that removal efficiency decreases as the input loading increases, and the tread-line reaches a plateau (>90% removal efficiency) when the input loading was below 0.01 g-Cu/g-Fe•h. To obtain a high removal efficiency (>90%), input loading should be maintained below 0.01 g-Cu/g-Fe•h, which could be achieved by increasing iron concentration and/or HRT. The input loading defined here can be used as a convenient master to quantify the impacts of parameter variations on the removal efficiency.

Removal capacity: The removal capacity of nZVI can be calculated by dividing the total mass of Cu(II) retained by the total amount of nZVI applied to the reactor:

$$\text{Removal capacity} = \frac{Cu_T^{in} - Cu_T^{out}}{Fe_T} \qquad \text{Unit: g-Cu/g-Fe} \qquad (2)$$

Where Cu_T^{in}, Cu_T^{out} and Fe_T stand for the total amounts of Cu(II) flow into/out the reactor, and total nZVI dosed during the entire period of a test, respectively. Results are presented in Table 1 and 2. The maximal removal capacity observed was 0.343 g-Cu/g-Fe at 1.25 m^3/h, much greater than the uptake capacity of conventional adsorbents or ion exchange materials[4] and ZVIs in packed columns and batch reactors.

Greater removal capacity of nZVI in this reactor was made possible by the continuous recycle of nZVI, via a sedimentation unit after the nZVI reactor. A solids recirculation pump drew the nZVI settled at the bottom of clarifier and piped it to front end of the nZVI reactor, and the nZVI recirculating configuration was similar to those used in traditional returned activated sludge. The rationale for recycling is that nZVI after the first pass of use still possesses considerable reactivity and Fe(0) for subsequent uses. In the absence of strong oxidants, complete oxidation of nZVI in aqueous environment may take a much longer time (hours to days) than the HRT of nZVI reactor. Previous results suggested that the depletion of metallic iron content of bare nZVI may take 20 days, under neutral pH in deoxygenated DI water.[21] Doping of metals like Ni, Cu and Ag on nZVI may accelerate the corrosion of nZVI in water. For example, 0.1% (w/w) Cu or Pd decreased the anticipated longevity of nZVI to 12 days and 20 hours, respectively, but these timeframes are still much longer than most HRTs of conventional reactors. Tests with repeatedly spiked pollutants revealed that nZVI remained reactive after several trials, even with hexavalent chromium (Cr(VI)), whose reduced form (Cr(III)) is known to cause ZVI passivation.[22] The same observation has been recorded during repetitive loadings of Cu(II) on nZVI.[13] Due to the galvanic effects, reduced copper cemented on nZVI may accelerate the reaction of the remaining metallic iron until all the ZVI content is depleted. Recycling nZVI thus prolongs the retention time of nZVI in the reactor, increases the utilization efficiency of nZVI and thus reduces treatment cost. Lastly, intensive mechanical mixing may have contributed to the high removal capacity as well. Continuous agitation of the nZVI suspension reduces the precipitation of corrosion products on the particle surfaces, thus mitigating particle passivation to some extents and making the entire metallic iron content more accessible for Cu(II) reduction.

<u>Solution chemistry of the Cu(II)-nZVI reactions:</u> Table 1 presents average pH values of the influent and nZVI suspension in the reactor. Average pH of the influent was in the range of 3.9-5.4. Under this pH, it was expected that dissolved cupric ion was the dominant form of copper. pH of nZVI suspensions in the reactor was elevated to 5.7-6.9, due to the corrosion of iron by water which consumes protons:[12]

$$Fe^0\,(s) + 2H^+ \rightarrow Fe^{2+} + H_2\,(g) \qquad (3)$$

The presence of nZVI also led to decreased solution E_h. An interesting result came from the average E_h values of nZVI suspensions at different flow rates (Figure 4a). While average influent E_h was near constant at around +400 mV, E_h of nZVI suspension (reactor E_h) rose as flow rate increased. Average suspension E_h at 1.0 m^3/h was -53 mV and ascended to +258 mV at 2.5 m^3/h. The measured E_h of nZVI suspensions was in fact the combined effects by a number of redox couples in the solution/suspension.[23] In this particular case, the couples involved were Fe(II)/Fe, Cu(II)/Cu, Fe(III)/Fe(II), H^+/H_2, O_2/OH^-. At higher flow rates, more oxidant species such as Cu(II) were left in the suspension, as shown in Table 1 and Figure 2a. Higher concentrations of oxidants in the suspension manifest themselves in higher E_h values via coupled equilibrium with electrode-sensitive redox couples. Since solution pH and operational conditions (e.g., nZVI dose) were similar at different flow rates, the proton and oxygen concentrations were expected to be similar among different tests, so the variations in E_h were mainly caused by changes in Cu(II) concentration. This point is more evident in Figure 4b, which depicts a strong correlation between suspension E_h and the residue Cu(II) concentrations in the solutions during different pilot tests. Generally, high solution E_h implicates higher Cu(II) content in the solutions. As solution E_h can be easily monitored with an electrode, the correlation suggests that the E_h of nZVI suspension could function as an indicator of reactor performance, bringing convenience and flexibility to the reactor operation, especially in coping with industrial wastewater whose characteristics tend to fluctuate considerably with time. Precautionary measures, such as feeding the reactor with more nZVI, could be taken immediately after the reactor E_h reaches a preset value, avoiding the direct discharge of a poorly treated effluent. In comparison, fixed-bed reactor configurations do not offer such flexibility.

Chemistry of Cu(II) removal by nZVI

To investigate the reaction mechanisms amid the fluctuations and impurities of the industrial wastewater from a field operation is challenging. Laboratory batch tests (Figure 5) were conducted using nZVI slurry and lab-prepared Cu(II) solutions to gain insights into the Cu(II) removal by nZVI. All solutions were prepared in deionized water. The batch reactors were repeatedly spiked with a fixed amount of concentrated Cu(II) solution (32 ml, 12 g-Cu(II)/L), which was to simulate the continuous input of pollutants into the reactor in the pilot system. Each spike amounted to a net increase of Cu(II) concentration of 384 mg/L in the flask and the accumulative input was 2,688 mg/L (Figure 5). Results indicated rapid sequestration of cupric ions from the solution, leaving less than 0.1 mg/L Cu(II) in the solution after 30 minutes in the first few trials. After 6th and 7th spikes, 10 mg/L and 28 mg/L Cu(II) remained in the solution, suggesting the reduction capacity of nZVI was nearly exhausted (Figure 5a). In sum, 2,660 mg/L Cu(II) was removed, generating a total removal capacity of 1,330 mg-Cu/g-nZVI. The large capacity of nZVI stems from the nature of Cu(II)-Fe(0) reactions: different from ion-exchange and adsorption processes whose capacities are determined by number of reactive sites at the solid-liquid interface, Cu(II) removal by nZVI is a redox reaction in which the entire metallic iron content is accessible by the reaction. The metallic iron core of nZVI possesses a large capacity for the Cu(II) reduction.[24] Assuming that all the cupric ions are reduced to metallic copper following equation 4 in which cupric ion and iron are reacted as 1:1 molar ratio,

$$Cu^{2+} + Fe^{0} \rightarrow Cu^{0} + Fe^{2+} \qquad (4)$$

Then the maximum removal capacity of nZVI should be 948 mg-Cu/g-nZVI. Due to the oxidation of metallic iron, only a fraction (~83%, w/w) of nZVI is in the form of metallic iron, thus the removal capacity by reduction alone is expected to be substantially lower than 948 mg-Cu/g-nZVI. However, the observed removal capacity in this test, 1,330 mg-Cu/g-nZVI, is 40% greater than the theoretical value based on chemical reduction. This suggests that the Cu(II) removal may be caused by more than one reaction. As presented below, XRD analysis shows that Cu(II) can also be reduced to Cu_2O, which has a Cu(II)/Fe(0) stoichiometry of 2:1. This means that one mole of iron can reduce up to 2 moles of Cu(II) and thus results in higher removal capacity.

The changes in Cu(II) concentration were mirrored by the solution E_h trends. Figure 5b delineated the E_h profiles of two separate batches. A sharp decrease in E_h, from +300 mV to -560 mV, was observed upon addition of 2 g/L nZVI in 3 minutes. Spiking of Cu(II) led to instantaneous increase of solution E_h, indicating free Cu(II) plays an important role in determining E_h of nZVI slurry. As discussed in the previous section, Cu(II) is a relatively strong oxidant and thus responsible for the surge of solution E_h. Nonetheless, in the first few trials the impact of Cu(II) on solution E_h was quickly annihilated, and solution E_h fell back to -500 mV in 30 min. The receding of solution E_h can be attributed to the decreasing level of aqueous Cu(II), as verified by the data presented in Figure 5a. When most of the aqueous Cu(II) was sequestrated by nZVI, Fe(II)/Fe became the dominant couple in determining the measured E_h again, until interrupted by the next round of spiked Cu(II). Therefore, it can be concluded that solution E_h could be used to evaluate the extent of Cu(II) removal by nZVI.

Characterizations of reacted nZVI

Changes of nZVI after the reactions with Cu(II) were examined with high-resolution SEM (Figure 6). Fresh nZVI has a spherical shape with diameters spanning from 50 to

150 nm (Figure 6a-b). The particles were connected in one-dimensional chains likely due to magnetic dipole interactions and chemical aggregation.[26] After reactions with Cu(II), nZVI displayed a drastically different morphology as shown in Figure 6c. Numerous dendritic deposits were observed growing on chunky, irregular-shaped bases. Close-up view in Figure 6d revealed that the deposits showed preferential directions of growth and formed rod-like shapes that were indicative of crystalline structures. Some rods branched out into parallel arms, giving rise to fishbone-like arrangement. The bases appear to comprise of multitude of smaller particles fusing together. The shapes of the individual particles were less distinguishable compared to fresh nZVI particles. Surface elemental composition was analyzed with EDS scan at an area populated with dendritic deposits. As shown in Figure 6e, strong signals corresponding to Cu were detected, which confirmed that the dendritic deposits were mostly reduced copper. The clusters of particles underneath the deposits were believed to be products of nZVI oxidation. Rapid corrosion of iron in solution caused accumulation of Fe(III) hydroxides on particle surface, which held the particles together to create lumpy aggregates several microns in size (Figure 6d).

The morphology of Cu deposits on iron or other sacrificial metals has been reported to be related to reaction kinetics.[27-29] Fast kinetics causes numerous crystalline Cu nuclei to precipitate on the surface at the onset of the reaction. Since copper is a more efficient cathode surface than iron, these nuclei sites accelerate the reaction and promote the formation of fine, loose dendrites. In contrast, copper deposits in the form of a dense and smooth layer over the sacrificial metal are associated with slow reactions. Thus, the fine-textured copper deposits observed in this work manifest the rapid reaction between nZVI and Cu(II).[28,29]

XRD analysis of nZVI: To determine the composition of the reaction products, XRD analyses were performed with fresh nZVI and reacted nZVI from both batch and pilot reactors. As shown in Figure 7a, α-Fe was found in the fresh nZVI. Several new peaks emerged in the XRD patterns of the reacted nZVI after several recycling loops from one of the pilot tests (Figure 7b). They were identified as Cu_2O and Cu. XRD of batch tests solids (Figure 7c) also suggested the same products. Both results indicated that Cu(II) was reduced to metallic copper and cuprite following equations 4 and 5:

$$Fe^0 + 2Cu^{2+} + H_2O \rightarrow Fe^{2+} + Cu_2O + 2H^+ \quad (5)$$

From Equation 5, Cu(II) is reduced to cuprite at a Fe to Cu molar ratio of 1:2, and this may partially explain the high reduction capacity of 1330 mg-Cu/g-Fe observed in the batch experiments. No other peak except those of copper and cuprite were found in the batch precipitates, suggesting complete exhaustion of metallic iron. Copper in the metallic or cuprite form is less bioavailable than that from $Cu(OH)_2$ or CuS generated by chemical precipitation,[1] meaning more stable products generated by the nZVI reduction.

The recycled nZVI by the end of each test was digested using nitrate and perchloric acids for metal content analysis. Results revealed that more than 10% (w/w) of recycled nZVI was Cu (Table1). The highest Cu content was found in the sludge from the 1.0 m^3/h test, in which Cu contributed to 25% of the solid mass. These results were consistent with the high removal efficiency observed (343 mg-Cu/g-Fe). Cu contents in these recycled nZVI were 30 times greater than those in typical copper ores (average grade < 0.6%), and also much greater than Cu in the solid residues from fixed-bed reactors. Cu content in recycled nZVI can be further enriched by acid washing. Figure 7d presents the XRD spectrum of recycled nZVI after washing by hydrochloric acid. After acid washing, metallic iron peaks disappeared completely. Considering only 4% of Cu(II) escaped at 1.0 m^3/h, this nZVI reactor has the potential for recovering heavy metals from wastewater.

Cost of the nZVI process

A general concern of nZVI technologies is the treatment cost. The recirculation and reuse of nZVI in the treatment process increase the material efficiency and reduce the nZVI dosage. The construction cost of this process is also low due to the simple design and short reaction time. Operations of nZVI reactor require less labor-costing procedures as the control parameters are well defined and easy to monitor and regulate. The end product also contains high level of valuable metals and can offset the treatment cost. Furthermore, we have introduced a cost-effective method for large-scale nZVI production, which further brings down the cost of nZVI.[30]

Conclusions

nZVI was applied for treatment of wastewater containing high levels of Cu(II). A CFSTR reactor, in conjunction with a clarifier and a nZVI recirculation system, was developed to achieve high removal efficiency and high nZVI utilization. The reactors were tested on pilot scale to treat printed circuit board manufacturing wastewater which contained approximately 70 mg/L Cu(II), at flow rates from 1.0 to 2.5 m^3/h. Approximately 55 kg nZVI was consumed and a total of 250,000 L of wastewater was treated. This pilot-scale system achieved Cu(II) removal efficiency greater than 96%. nZVI material efficiency was greatly improved by this CFSTR system with a recycling loop. Results demonstrated outstanding performance of the reactor in several aspects, including high removal efficiency, reduced hydraulic retention times (1.6 h), elevated volumetric loading rates (ca. 1876 g-Cu/m^3•d) and a large Cu(II) removal capacity (343 mg-Cu/g-Fe). A strong correlation between suspension E_h and Cu(II) concentration in the reactor provides a convenient tool to monitor Cu(II) removal efficiency and adjust nZVI dose. This affords good operation control in coping with dynamic streams from industrial processes. High Cu content (up to 25% w/w) in the reacted solid residues suggests this treatment configuration could potentially be applied for recovering valuable metals from industrial wastewater.

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Table 1 Major parameters of nZVI reactor

Influent					Reactor				Effluent			Recycled nZVI
Q (m^3/h)	pH^a	$[Cu(II)]^a$ (mg/L)	TQ (m^3)	Cu_T^{in} (kg)	HRT (h)	Fe_T (kg)	nZVI dose (g/L)	pH^a	$[Cu(II)]^a$ (mg/L)	Cu_T^{out} (kg)	Cu Removed (kg)	Cu content (mg-Cu/g)
1.00	3.9	52.5	65	3.41	1.6	15.0	0.23	6.8	1.7	0.11	3.30	252
1.25	5.3	89.2	43	3.84	1.3	10.0	0.23	5.7	9.5	0.41	3.43	189
1.50	4.8	93.9	45	4.23	1.1	10.0	0.22	6.9	24.8	1.12	3.11	120
2.00	5.3	62.6	54	3.38	0.8	10.0	0.19	6.0	22.6	1.22	2.16	
2.50	5.4	68.1	43	2.89	0.6	10.0	0.22	5.7	49.8	2.12	0.77	

a: average.

Q: volumetric flow rate (m^3/h).

TQ: total influent volume (m^3).

HRT: hydraulic retention time (h).

Cu_T^{in}: total Cu(II) flow into the reactor (kg).

Fe_T: total nZVI dosed during the entire period of a test (kg).

Cu_T^{out}: total Cu(II) flow out the reactor (kg).

Table 2 Comparison of different ZVI reactors for Cu(II) removal

Reactor		ZVI		Wastewater		Performance			Ref.
Type	Volume (ml)	Type	Mass (g)	Type	[Cu(II)] (mg/L)	HRT (h)	Removal capacity (g-Cu/g-Fe)	Volumetric loading rate (g-Cu/m^3•d)	
CFSTR	1,600,000	nZVI (30 m^2/g)	55,000	PCB industrial wastewater	73	1.3-1.6	0.343	1876	This study
Packed column	844	ZVI (0.05 m^2/g)	483	$CuSO_4$ solution	5, 50	6.8-34	0.029	10	9
Packed column	1963	ZVI	240	$Cu(NO_3)_2$ solution	500	15	0.087-0.106	194	18
Repetitive batch	50	nZVI (40 nm)	< 10	$Cu(NO_3)_2$ solution	10-500	4	0.25		13
Batch	2000	mZVI (0.3 m^2/g)	37.5	Acid rock drainage	138-146	3.3	0.0049		7

Figure captions

Figure 1 (a) A standard shipping container in which pilot reactors were placed; (b) a photo of the nZVI reactor; (c) nZVI suspension in the reactor; (d) process flow chart of the pilot test.

Figure 2 Performance of nZVI reactor at different flow rates.

Figure 3 Removal efficiency of nZVI reactor as a function of input Cu(II) loading (L).

Figure 4 (a) E_h of influent and nZVI suspension (at reaction zone) at different flow rates; (b) E_h of nZVI suspension as a function of aqueous Cu(II) (pilot tests). nZVI doses at different flow rates: 0.19-0.23 g/L.

Figure 5 Cu(II) removal by nZVI. (a) A batch flask containing 2 g/L nZVI was spiked repeatedly with Cu(II) solution until the reductive capacity was exhausted; (b) E_h of nZVI slurries with and without spiked Cu(II).

Figure 6 SEM images of nZVI particles. (a)-(b) pristine nZVI; (c)-(d) by the end of Cu(II) spiking batch test; (e) EDS spectrum of the reacted particles with inset showing the area subject to EDS scan.

Figure 7 XRD of pristine nZVI (a); Recycled nZVI (b); Precipitate recovered by the end of spiking batch test (c); Acid-washed recycled nZVI (d).

Figure 1

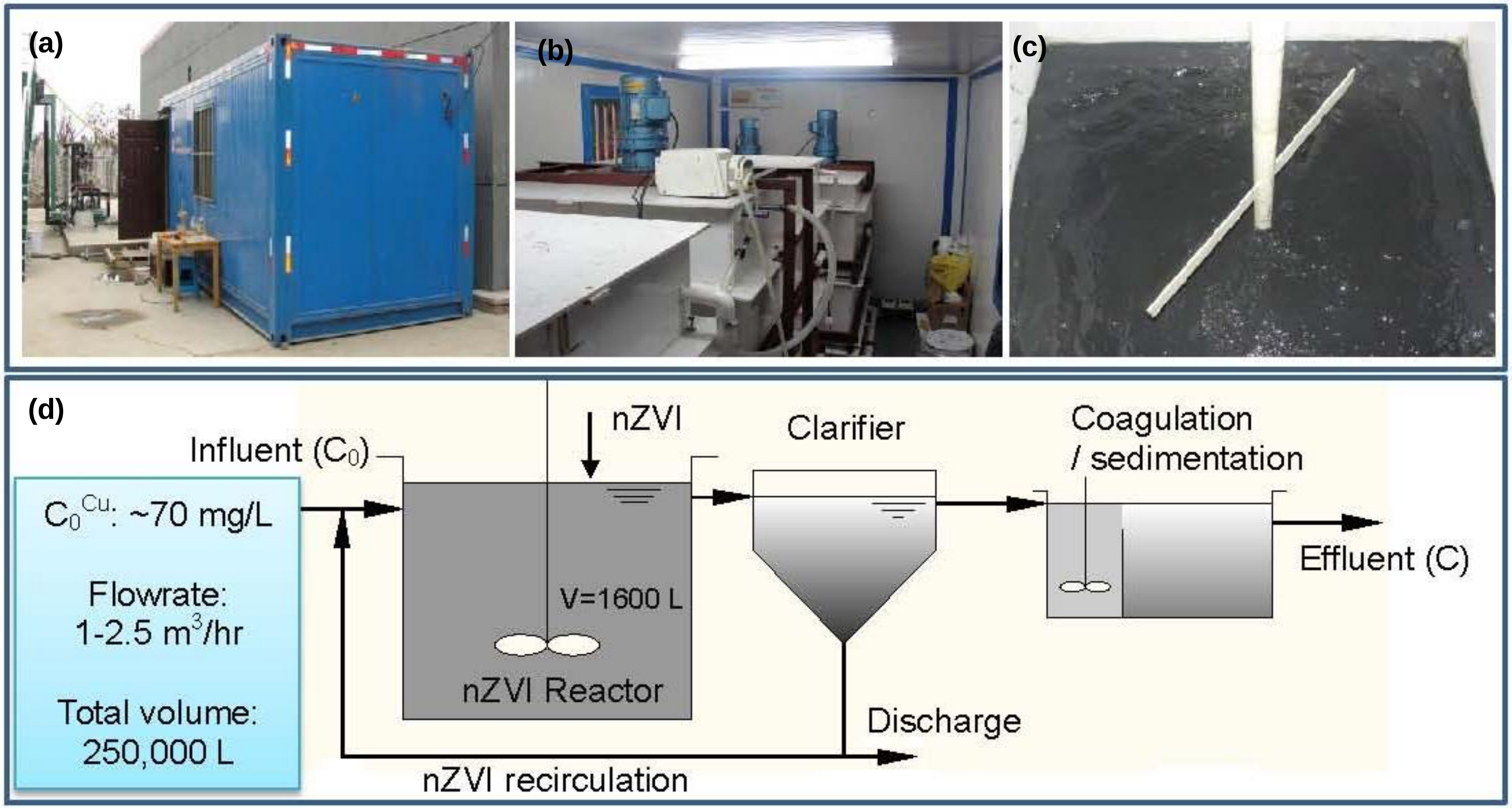

(a)
(b)
(c)
(d)
Influent (C_0)
nZVI
Clarifier
Coagulation / sedimentation
C_0^{Cu}: ~70 mg/L
Flowrate: 1-2.5 m^3/hr
Total volume: 250,000 L
V=1600 L
nZVI Reactor
Effluent (C)
Discharge
nZVI recirculation

Figure 2

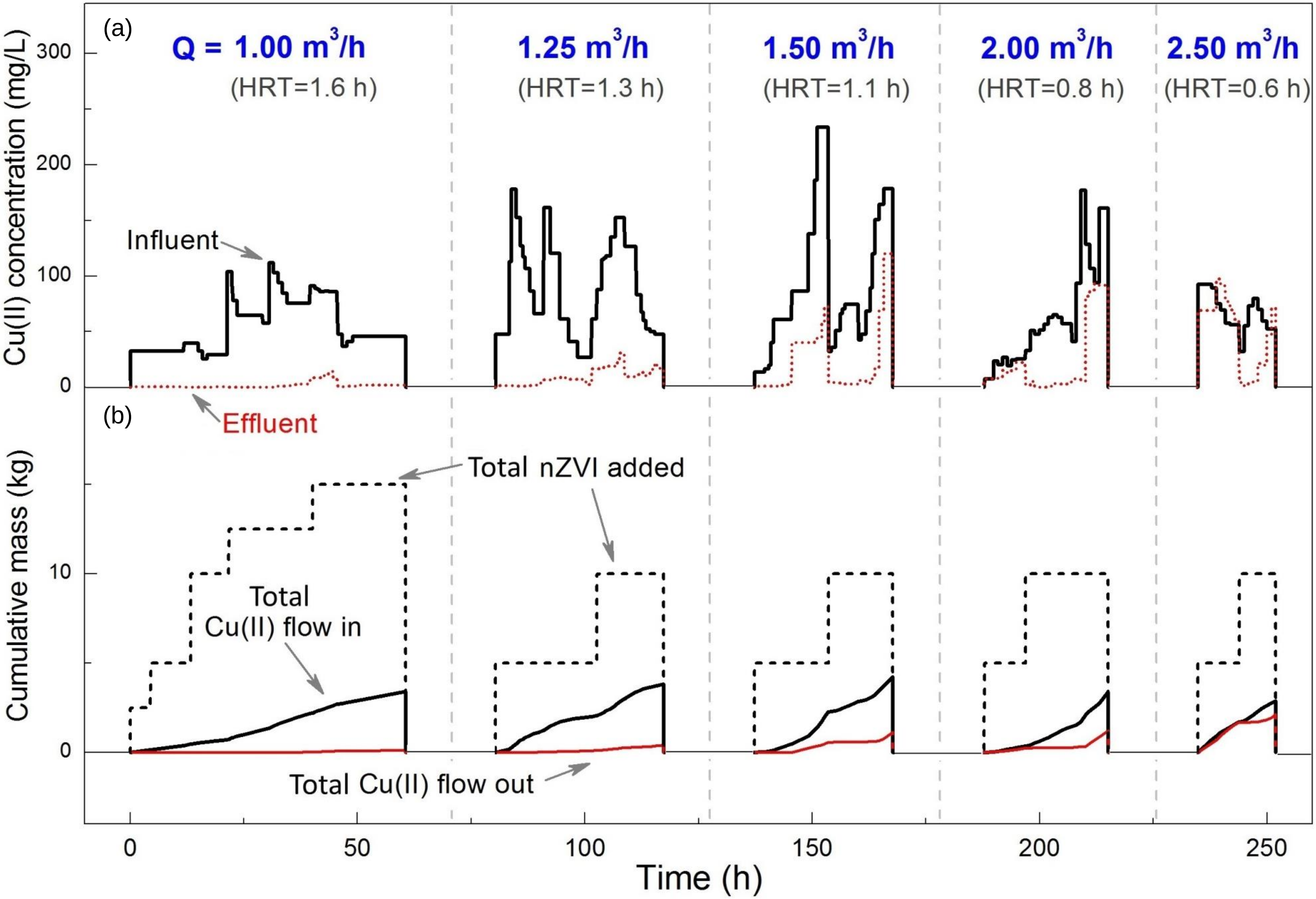

(a)
Q = 1.00 m³/h
(HRT=1.6 h)
1.25 m³/h
(HRT=1.3 h)
1.50 m³/h
(HRT=1.1 h)
2.00 m³/h
(HRT=0.8 h)
2.50 m³/h
(HRT=0.6 h)
Cu(II) concentration (mg/L)
300
200
100
0
Influent
Effluent
(b)
Total nZVI added
Total
Cu(II) flow in
Total Cu(II) flow out
Cumulative mass (kg)
10
0
0
50
100
150
200
250
Time (h)

Figure 3

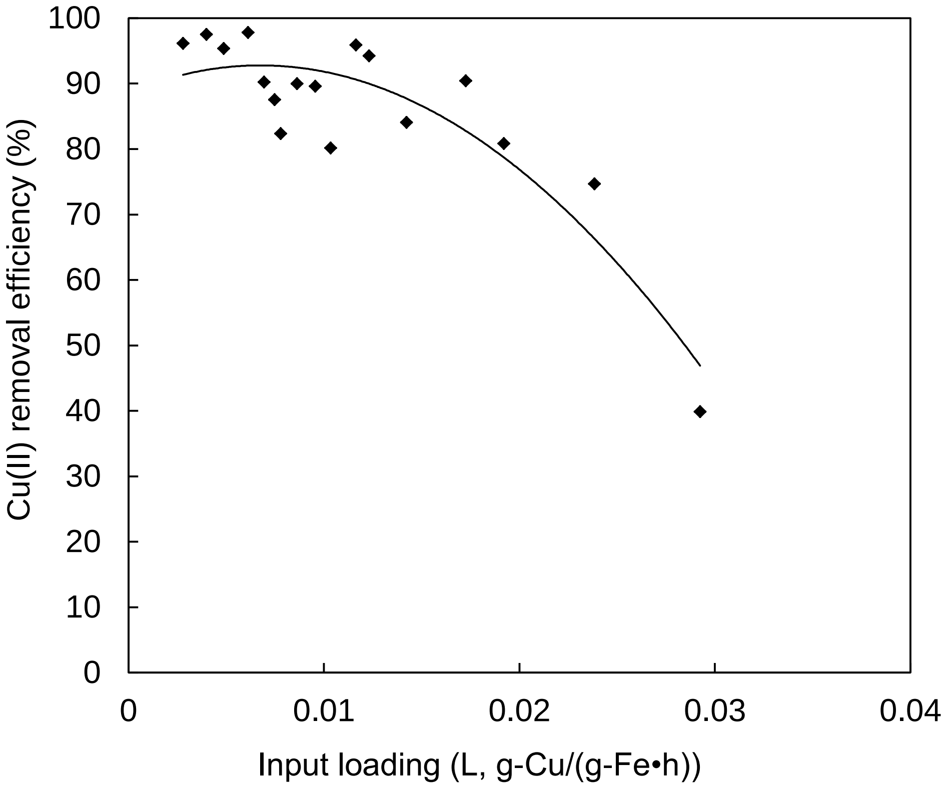

100
90
80
70
60
50
40
30
20
10
0
0
0.01
0.02
0.03
0.04
Cu(II) removal efficiency (%)
Input loading (L, g-Cu/(g-Fe•h))

Figure 4

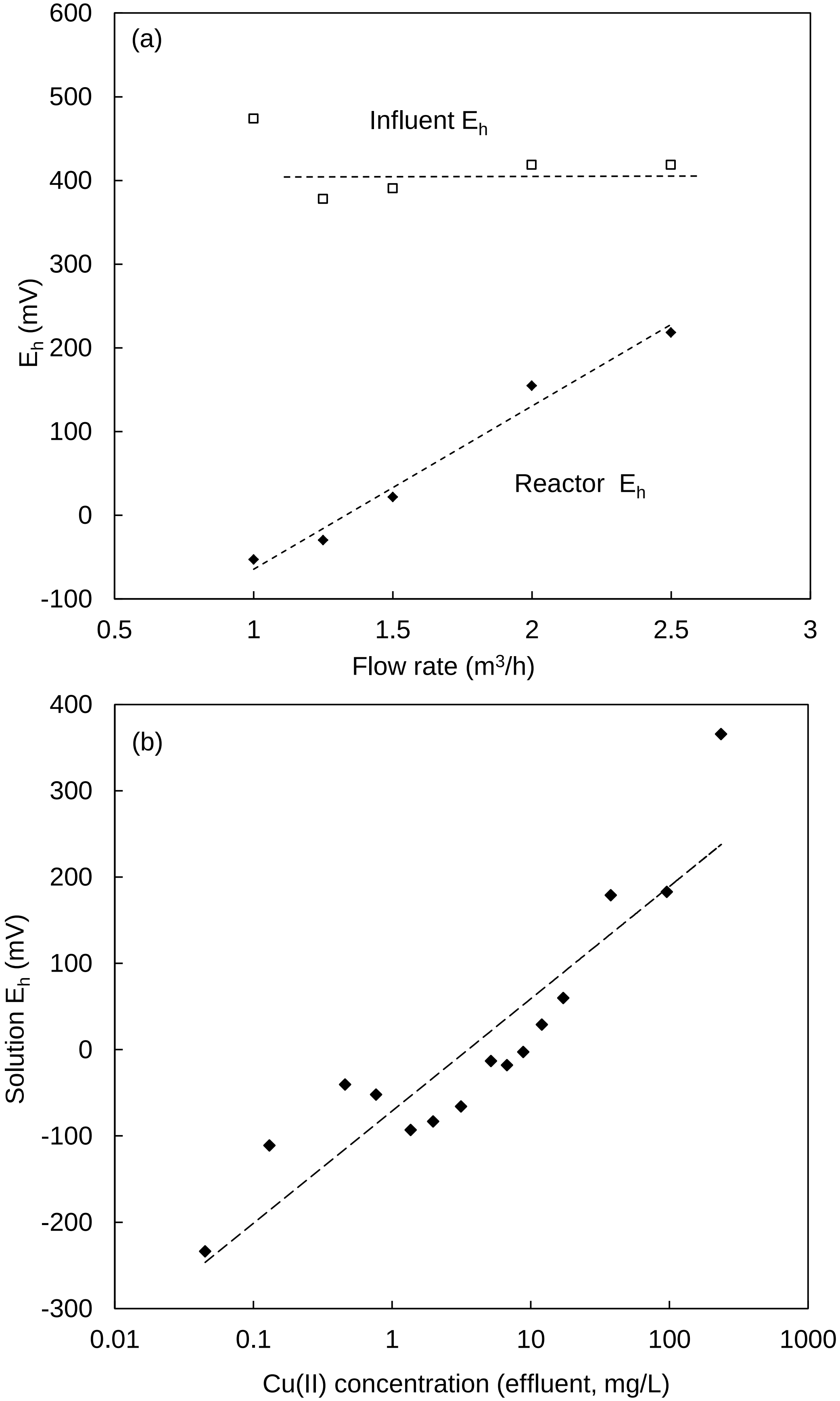

(a)
600
500
400
300
200
100
0
-100
E_h (mV)
Influent E_h
Reactor E_h
0.5
1
1.5
2
2.5
3
Flow rate (m^3/h)
(b)
400
300
200
100
0
-100
-200
-300
Solution E_h (mV)
0.01
0.1
1
10
100
1000
Cu(II) concentration (effluent, mg/L)

Figure 5

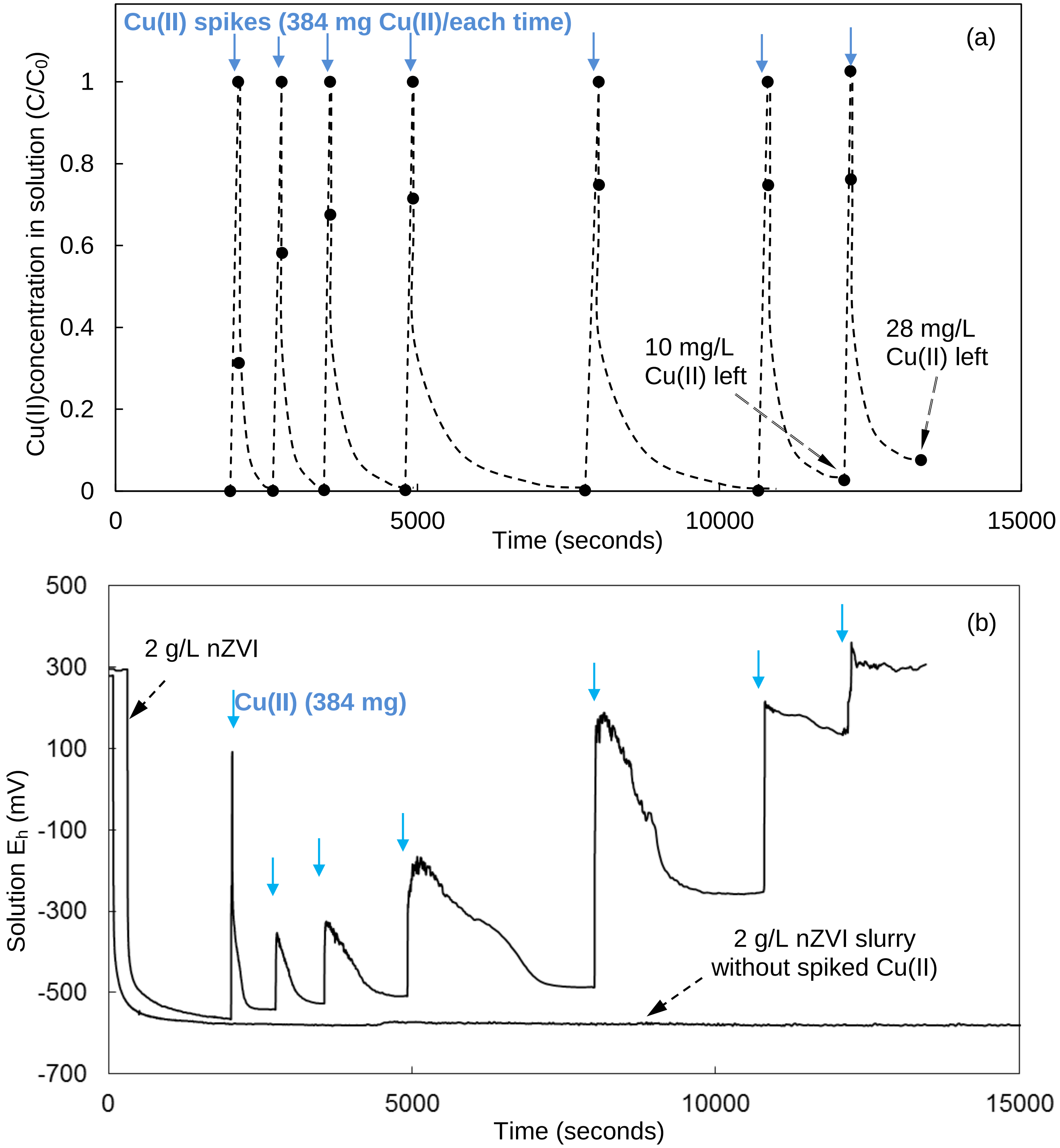

Cu(II) spikes (384 mg Cu(II)/each time)
(a)
Cu(II)concentration in solution (C/C0)
1
0.8
0.6
0.4
0.2
0
10 mg/L
Cu(II) left
28 mg/L
Cu(II) left
0
5000
10000
15000
Time (seconds)
500
300
100
-100
-300
-500
-700
(b)
2 g/L nZVI
Cu(II) (384 mg)
Solution Eh (mV)
2 g/L nZVI slurry
without spiked Cu(II)
0
5000
10000
15000
Time (seconds)

Figure 6

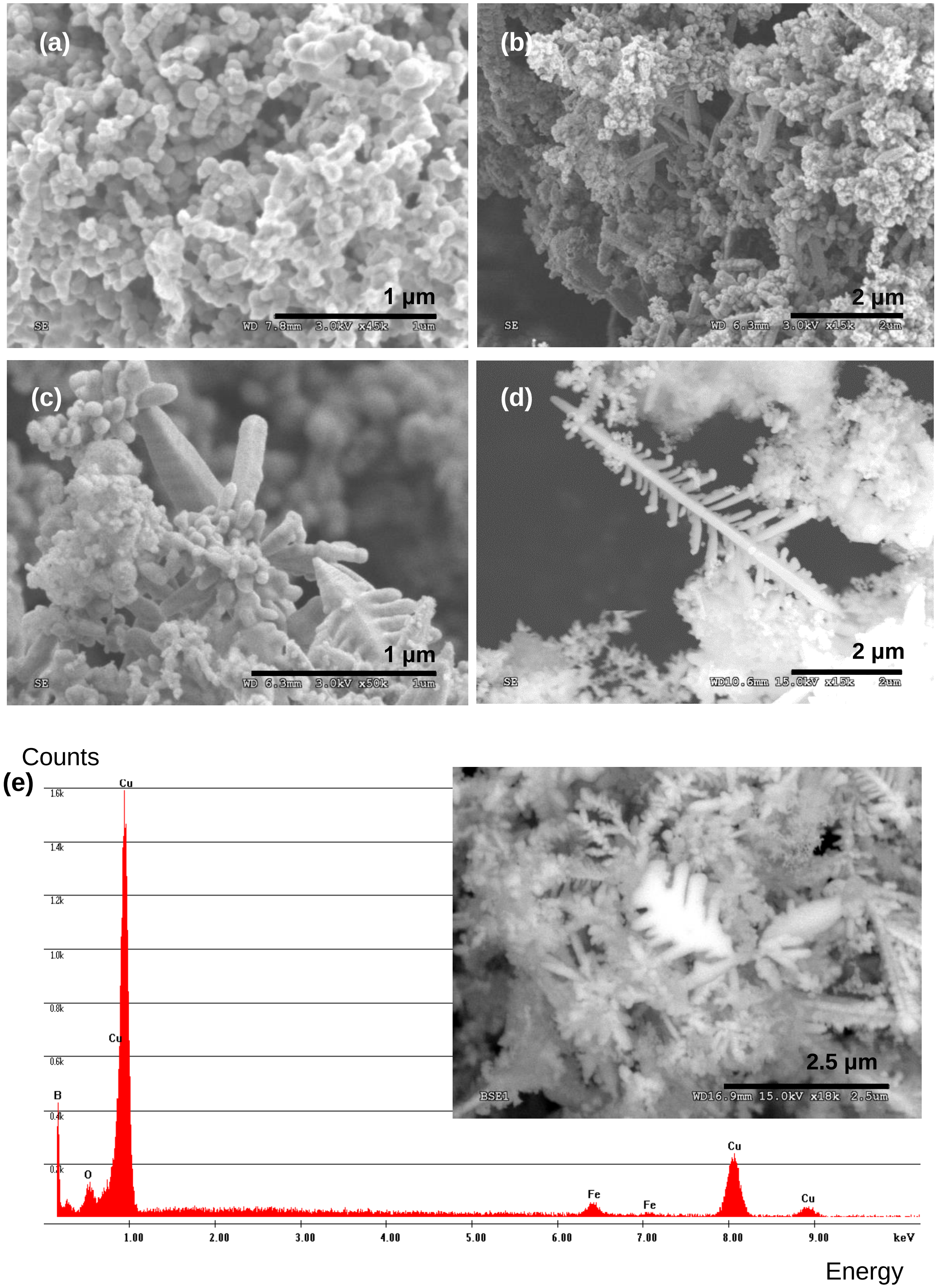
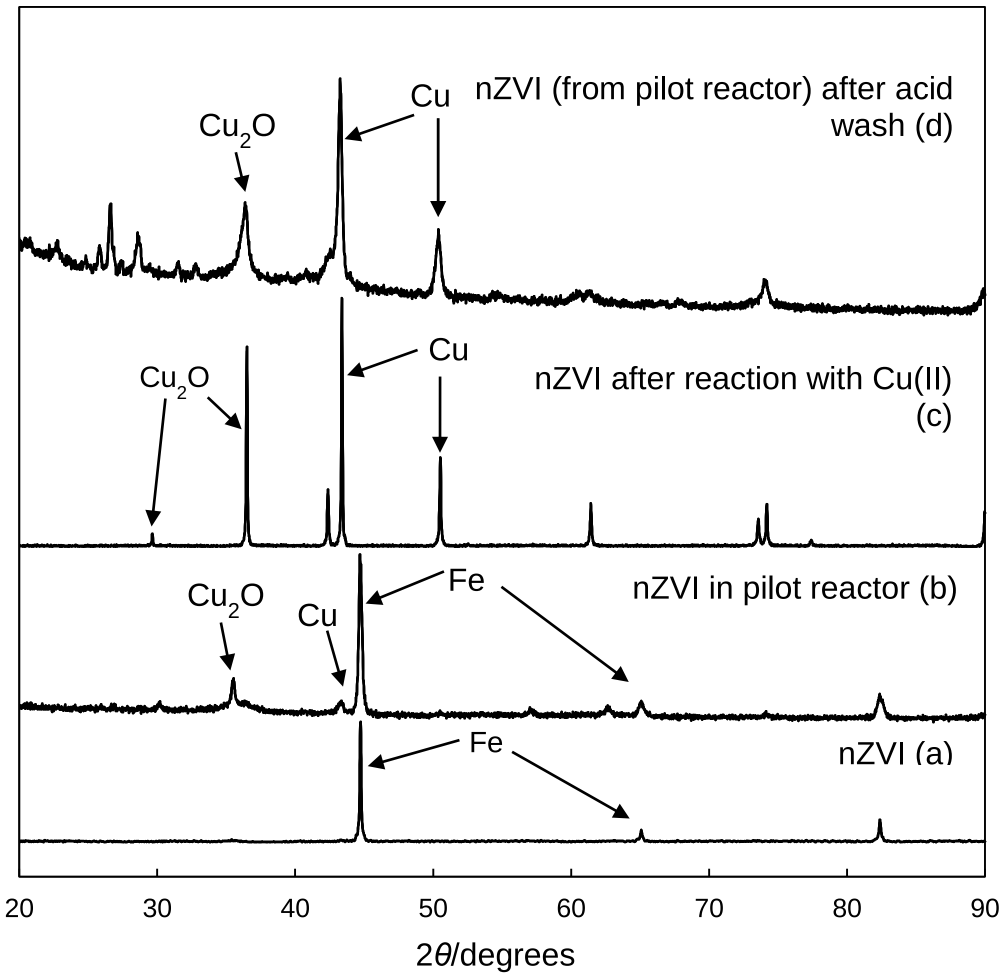

(a)
1 µm
SE
WD 7.8mm 3.0kV x45k 1um
(b)
2 µm
SE
WD 6.3mm 3.0kV x15k 2um
(c)
1 µm
SE
WD 6.3mm 3.0kV x50k 1um
(d)
2 µm
SE
WD10.6mm 15.0kV x15k 2um
Counts
(e)
1.6k
1.4k
1.2k
1.0k
0.8k
0.6k
0.4k
0.2k
Cu
Cu
B
O
Fe
Fe
Cu
Cu
2.5 µm
BSE1
WD16.9mm 15.0kV x18k 2.5um
1.00
2.00
3.00
4.00
5.00
6.00
7.00
8.00
9.00
keV
Energy

Figure 7


nZVI (from pilot reactor) after acid wash (d)
Cu
Cu_2O
nZVI after reaction with Cu(II) (c)
Cu
Cu_2O
nZVI in pilot reactor (b)
Fe
Cu_2O
Cu
nZVI (a)
Fe
20
30
40
50
60
70
80
90
2θ/degrees