# Premagnetization for Enhancing the Reactivity of Multiple Zerovalent Iron Samples toward Various Contaminants

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**S** *Supporting Information*

**ABSTRACT:** Premagnetization was applied to enhance the removal of various oxidative contaminants (including amaranth (AR27), lead ion ($Pb^{2+}$), cupric ion ($Cu^{2+}$), selenite ($Se^{4+}$), silver ion ($Ag^+$), and chromate ($Cr^{6+}$)) by zerovalent iron (ZVI) from different origins under well-controlled experimental conditions. The rate constants of contaminants by premagnetized ZVI (Mag-ZVI) samples were 1.2−12.2-fold greater than those by pristine ZVI (Pri-ZVI) samples. Generally, there was a linear correlation between the specific reaction rate constants ($k_{SA}$) of one particular contaminant removal by various Pri-ZVI or Mag-ZVI samples and those of the other contaminant, which could be successfully employed to predict the $k_{SA}$ of one contaminant by one ZVI sample if $k_{SA}$ of the other contaminant by this ZVI sample was available. The specific rate constant of Fe(II) release at pH 4.0 was proposed in this study to stand for the intrinsic reactivity of a ZVI sample. All Mag-ZVI samples had higher intrinsic reactivity than their counterparts without premagnetization. There were strong correlations between the intrinsic reactivity of various Pri-ZVI/Mag-ZVI samples and the removal rate constants of a specific contaminant by these ZVI samples not only at pH 4.0 when the intrinsic reactivity was determined but also at other pH levels. This correlation could be employed to predict the removal rate constant of this contaminant by a ZVI sample that was not included in the original data set once the intrinsic reactivity of the ZVI sample was known.
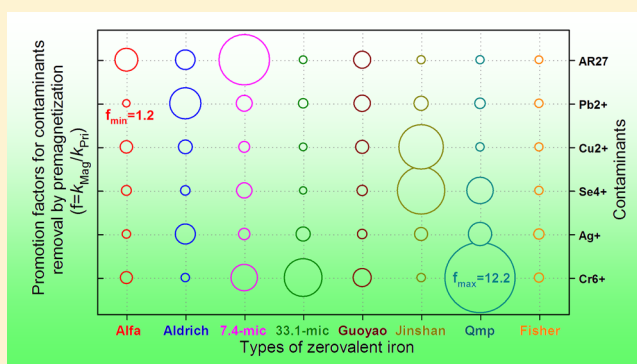
## INTRODUCTION

A wide range of organic and inorganic contaminants have been successfully removed from the aqueous phase by zerovalent iron (ZVI).[1−6] In these studies, there are numerous variables in the processes of contaminants removal by ZVI, for example, the type of contaminant,[2,7] condition of ZVI,[8−10] solution chemistry,[5,11−13] and hydrodynamic operating conditions.[8,14,15] A large number of scientists have addressed the influence of the individual factor on pathways,[16] kinetics,[5,12,15] and the mechanisms of contaminants sequestration by ZVI,[5,17] but only a few attempted to explore the relationships among these variables in contaminants elimination by ZVI.[2,3] In environmental science, correlation analysis typically involves regression of substrate property or reactivity data (defined as the response variable) for a series of related compounds with one or several convenient descriptor variables.[1,3] The resulting linear free energy relationship (LFER) can then be used to estimate values of reactivity for compounds that were not included in the original data set. Therefore, correlation analysis, an important tool for data validation and mechanistic investigations, is clearly a need for understanding the relationship between the degradation rates of the contaminants and the variability in reaction system from a broad perspective. The research group of Professor Tratnyek pioneered the correlation analysis of rate

constants of contaminants sequestration by ZVI.[1,3,18] Several studies have identified the molecular structural factors of chlorine-bearing compounds governing the surface area-normalized rate constants for dechlorination by ZVI, which included the energy of the lowest unoccupied molecular orbital ($E_{LUMO}$), and vertical attachment energies (VAEs).[1,3,19,20] Moreover, Miehr et al.[3] investigated the reactions of eight model contaminants (including cations, anions and neutral species) with nine types of granular ZVI in batch experiments and revealed that the reactivity of ZVI toward these contaminants generally decrease with increasing $E_{LUMO}$ and increasing chemical hardness of contaminants. However, they did not identify the role of ZVI's property in determining the reactivity of ZVI from different origins toward one specific contaminant. Tratnyek and his colleagues noticed that the rate of contaminant reduction by iron appeared to be first order with respect to the amount of metal available to serve as reductant and thus they proposed surface area-normalized rate constant ($k_{SA}$).[2] Hereafter, little progress had been made

**Table 1. Summary of the Properties of the ZVI Samples Employed in This Study**

| name | product/lot#/date | sample history | size/$d_{50}$, $\mu$m | SSA/m$^2$ g$^{-1}$ | Raman[a] | $M_R$*/emu g$^{-1}$ | $k_{\text{Fe(II) release SA}}$/mg m$^{-2}$ min$^{-1}$ | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | Pri-ZVI | Mag-ZVI |
| Alfa | 00737/H22 × 008/none | stored in N$_2$ | 46.2 | 0.47 | GOE | 0.48 | 7.70 | 8.89 |
| Aldrich | 12310/SZBD1070 V/none | stored in N$_2$ | 108.2 | 0.01 | GOE | 0.44 | 264.00 | 312.00 |
| 7.4-mic | none/none/none | stored in N$_2$ | 7.4 | 0.30 | HEM/LEP/MGN | 0.52 | 0.87 | 7.40 |
| 33.1-mic | none/none/none | aged in O$_2$ | 33.1 | 0.16 | GOE | 1.07 | 28.63 | 31.00 |
| Guoyao | 10011818/20120914/2012 | stored in N$_2$ | 40.5 | 0.15 | FXY/GOE/LEP/MGN | 0.48 | 1.47 | 27.73 |
| Jinshan | none/080208/2008 | stored in N$_2$ | 40.0 | 0.76 | FXY/GOE/HEM/MGN | 0.29 | 0.21 | 3.63 |
| Qmp | none/none/none | washed with DI-H$_2$O | 175.5 | 0.20 | HEM/LEP/MGN | 0.30 | 4.40 | 9.80 |
| Fisher | none/I60−500/none | stored in N$_2$ | 282.5 | 3.15 | AC/MGH/MGN | 3.16 | 0.28 | 0.62 |

[a]AC, FXY, GOE, HEM, LEP, MGH, and MGN stand for amorphous carbon, feroxyhyte, goethite, hematite, lepidocrocite, maghemite, and magnetite, respectively.

toward explaining the variability in reactivity among samples of ZVI from different sources.

It should be clarified that intrinsic reactivity is the fixed property for a specific ZVI sample and it is an invariable.[21] Moreover, the observed reactivity of a ZVI sample (the efficiency of contaminants removal by ZVI) is strongly dependent on various factors, including the properties of contaminants and the reaction conditions (pH, DO, dosage of ZVI, etc.).[22] The microsized ZVI generally has low intrinsic reactivity toward contaminants removal due to its inherent passive film and small surface area.[17] Various countermeasures for enhancing the reactivity of ZVI have been extensively investigated, including pretreatment of pristine ZVI to remove passive layer,[23−25] fabrication of nanosized ZVI to increase the surface area,[26] synthesis of ZVI-based bimetals taking advantage of the catalytic ability of the noble metal,[27] as well as the application of a weak magnetic field (WMF).[8,17,28,29] Nevertheless, those above-mentioned approaches bear some demerits, such as relatively complex procedures, extra costs (e.g., energy consumption, materials and placement), potential ecotoxicity and so on. Recently, we first reported that premagnetization could enhance the reactivity of ZVI toward As(III) sequestration.[30] Taking advantage of the magnetic memory of ZVI, the premagnetized ZVI (Mag-ZVI) can keep the remanence ($M_R$*) after the external magnetic field is withdrawn.[31,32] The memorized remanence makes each Mag-ZVI particle a small magnet, which generates an inhomogeneous magnetic field around the surface of Mag-ZVI particle, being analogous to the effect of WMF,[8,17,28,29] thus can enhance the performance of ZVI for contaminant removal. Compared to applying a weak magnetic field in a large treatment unit during the reaction, ZVI premagnetization is much easier to be applied since it takes only 1−2 min to magnetize ZVI before its application and this method can avoid the aggregation of ZVI particles. Considering that premagnetization is easy-operating, time-saving, chemical-free, and inexpensive, the influence of premagnetization on improving the reactivity of ZVI from different origins toward a wide range of environmentally important contaminants should be surveyed. When addressing the broad perspective of various contaminants removal by Mag-ZVI, heavy metals including chromium, lead, copper, selenium, and silver should be ranked in priority based on their toxicity and persistent characteristics.[33−35] In addition, the toxic synthetic dyes (e.g., azo dyes), posing a serious threat to both environmental and human health,[7,36] was also employed as a target contaminant in this study.

Accordingly, the major objectives of this study were to (1) explore the feasibility of premagnetization to enhance the reactivity of ZVI from various origins toward the removal of diverse contaminants; (2) determine the semiquantitative trends of sequestration kinetics for six contaminants by eight types of granular Pri-ZVI (stands for the pristine ZVI) and Mag-ZVI so as to estimate the performance of Pri-ZVI or Mag-ZVI toward one contaminant based on that toward another; (3) investigate the relationship between the rate constants for contaminants removal and the intrinsic reactivity of Pri-ZVI or Mag-ZVI samples to make more sensible recommendations for mitigating one particular contaminant.

## EXPERIMENTAL SECTION

**Materials.** All chemicals, purchased from Shanghai Qiangshun Chemical Reagent Company, were used as received. Six reductates investigated in this study included amaranth (99.0%), lead acetate (99.5+%), copper sulfate pentahydrate (99.0+%), sodium selenite (97.0+%), silver sulfate (99.0+%), and potassium bichromate (99.8+%). They will be referred to as AR27, Pb2+, Cu2+, Se4+, Ag+, and Cr6+, respectively, in the following text. The properties, including the conditional reduction potential and the molar magnetic susceptibility, of these chemicals are summarized in Supporting Information Table S1.

The eight types of granular ZVI used in this study were Alfa powder (Johnson Matthey Public Co. Ltd., Shanghai, +99.0%), Aldrich powder (Aldrich Chemical Co., Shanghai, +99.0%), Micrometer-scale ($d_{50}$ = 7.4 $\mu$m) powder (Beijing Dk Nano technology Co., Ltd.), Micrometer-scale ($d_{50}$ = 33.1 $\mu$m) powder (Beijing Dk Nano technology Co., Ltd.), Guoyao powder (Sinopharm Chemical Reagent Co., Ltd., Shanghai, +99.0%), Jinshan powder (Shanghai Jinshan reduced iron powder factory, Shanghai, +98.0%), Qmp powder (Quebec Metal Powders Ltd.) and Fisher filings (Fisher Scientific). Throughout the presentation of results that follows, these iron powders are referred to as Alfa, Aldrich, 7.4-mic, 33.1-mic, Guoyao, Jinshan, Qmp and Fisher, respectively. The SEM images, particle size distributions, Raman spectra, and small magnetic hysteresis loops of these iron samples are presented in Figures S(1−4) and the properties of these iron samples are summarized in Table 1.

**Batch Experiments.** The Pri-ZVI sample (0.25 g) enclosed in a zipper bag was magnetized in a uniform magnetic field

(MF) of 500 mT for 2 min and was denoted as Mag-ZVI hereafter. The static, uniform MF was generated by an electromagnet (Electromagnet Power Supply, model 7050), which was purchased from East Changing Technologies, Inc. (Beijing).

All stock solutions were prepared by dissolving the corresponding contaminants in ultrapure water generated from a Milli-Q reference water purification system. Working solutions were freshly prepared for each batch test by diluting the stock solutions. The initial pH value of the working solution was adjusted to 4.0 with 0.10 M NaAc-HAc as buffer, unless otherwise specified. The batch experiments investigating the kinetics of contaminants sequestration by Pri-ZVI/Mag-ZVI were performed open to the air and initiated by dosing 0.25 g Pri-ZVI/Mag-ZVI into a 0.50 L working solution with 0.20 mM $Na_2SO_4$ as background electrolyte and mixed at 400 rpm with a mechanical stirrer. The initial concentration of bichromate was 0.05 mM because of its passivating effect and that of other redutates was 0.20 mM. The intrinsic reactivity of a Pri-ZVI or Mag-ZVI sample was defined in this study as the specific Fe(II) release rate of 0.5 g $L^{-1}$ ZVI at pH 4.0 with 0.10 M NaAc-HAc as buffer and with 0.20 mM $Na_2SO_4$ as background electrolyte ($k_{Pri/Mag Fe(II) release SA}$). To be consistent, it should be emphasized that the mixture was mixed at 400 rpm with a mechanical stirrer in a wide-mouth bottle and the experiments were carried out open to the air to determine the intrinsic reactivity of a ZVI sample. Each experiment was performed in duplicate. The temperature of all the experiments in this study was controlled at $25 \pm 1$ °C with a water bath.

**Chemical Analysis and Solid Phase Characterization.** Samples of batch tests were collected at given time intervals using a 10 mL syringe, filtered immediately through a 0.22 $\mu$m membrane filter, and acidified for analysis. Concentrations of Pb2+, Cu2+, Se4+, and Ag+ were determined by ICP-AES, whereas those of Cr6+, AR27, and Fe(II) were analyzed with colorimetric methods using a UV−visible spectrophotometer. The concentration of Cr6+ was determined by monitoring the absorbance at 540 nm after reacting with diphenylcarbazide.[37] The concentration of AR27 was determined by measuring its absorbance at 521 nm, and that of Fe(II) was analyzed by the 1,10-phenanthroline colorimetric method at a wavelength of 510 nm.[7,38]

Morphological analyses of the ZVI samples from different sources were performed by scanning electron microscopy (SEM) using a Hitachi 4700 microscope (at 20 kV). The size distributions of the ZVI particles were examined by a size distribution analyzer (Bettersize 2000, Dandong Bettersize instruments Ltd., China). Raman spectra were collected using a DXR Raman Microscope (Thermo Fisher Scientific, Inc., China) with a 532 nm laser (2.0 mW), scanning from 100 to 1700 $cm^{-1}$ at room temperature. Specific surface area of the ZVI samples was determined by nitrogen adsorption using the BET method (Micrometrics ASAP 2020). The magnetic hysteresis loop measurements for various ZVI samples were carried out using a vibrating sample magnetometer (VSM, Lakeshore 7400, Lakeshore) at room temperature.

## RESULTS AND DISCUSSION

**Influence of Premagnetization on the Kinetics of Contaminants Sequestration by ZVI.** The raw kinetic data of contaminants (i.e., AR27, Pb2+, Cu2+, Se4+, Ag+, and Cr6+) removal from water by various Pri-ZVI/Mag-ZVI samples (i.e., Alfa, Aldrich, 7.4-mic, 33.1-mic, Guoyao, Jinshan,

Qmp and Fisher) are presented in Figure S5. Each cell in this matrix represents a combination of reductate and reductant and this figure shows all of the time courses that are used in subsequent kinetic analyses. Obviously, premagnetization enhanced the reactivity of ZVI of different origins toward various contaminants removal but to diverse extents and accelerated the corresponding Fe(II) release during the process of contaminants (i.e., $Pb^{2+}$, $Cu^{2+}$, $Se^{4+}$, and $Ag^+$) removal by Pri-ZVI/Mag-ZVI (Figure S6). To quantitatively describe the influence of premagnetization on the reactivity of ZVI, it was necessary to derive the rate constants from the kinetic data (Figure S5). Thus, the pseudo-first-order rate law (eq 1) was used to simulate the kinetics of contaminants elimination,[2] as illustrated by the dashed lines in Figure S5 and the obtained rate constants of contaminants removal by Pri-ZVI ($k_{Pri\ obs}$) and Mag-ZVI ($k_{Mag\ obs}$) are summarized in Figure 1.

$$\frac{d[contaminant]}{dt} = -k_{obs}[contaminant] \quad (1)$$

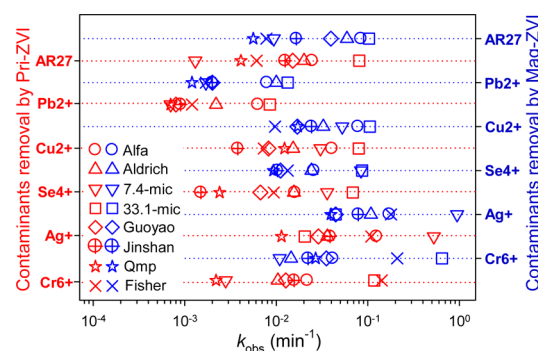where $k_{obs}$ is the pseudo-first-order rate constant ($min^{-1}$) of contaminant removal by ZVI.



**Figure 1.** Rate constants ($k_{obs}$, $min^{-1}$) of Cr6+, Ag+, Se4+, Cu2+, Pb2+, and AR27 sequestration by Pri-ZVI (left ordinate) and Mag-ZVI (right ordinate). Reaction conditions: $[Fe^0] = 0.50$ g $L^{-1}$, [NaAc-HAc] = 0.10 M (pH 4.0), [Intensity of MF for premagnetization] = 500 mT, $t_{premag}$ = 2 min, $T = 25 \pm 1$ °C.

The comprehensive perspective provided by Figure 1 reveals several broad trends in the data. First, the first-order rate constants ($k_{obs}$) of sequestering a particular contaminant by Pri-ZVI or Mag-ZVI from different origins vary by about 2 orders of magnitude. Second, premagnetization does increase the rate constants of the tested contaminants removal by all examined ZVI samples, although the improvement is different for different ZVI-contaminant combinations. As illustrated by the bubble plot in Figure S7, the rate constants of contaminants by Mag-ZVI samples were 1.2- to 12.2-fold greater than those by Pri-ZVI samples. Third, the rate constants for contaminants removal by both Pri-ZVI and Mag-ZVI generally follow the order Ag+ > Cr6+ > Cu2+ > AR27 > Se4+ > Pb2+. The mean value of rate constants were increased appreciably from 0.021 to 0.041 $min^{-1}$ for Ar27, from 0.003 to 0.005 $min^{-1}$ for Pb2+, from 0.025 to 0.042 $min^{-1}$ for Cu2+, from 0.020 to 0.033 $min^{-1}$ for Se4+, from 0.112 to 0.201 $min^{-1}$ for Ag+ and from 0.041 to 0.126 $min^{-1}$ for Cr6+, respectively, after the ZVI was premagnetized (Table S2). This ranking of relative reactivity, over such a diverse range of substrates, provides an expanded perspective on the reactivity of ZVI and the performances of
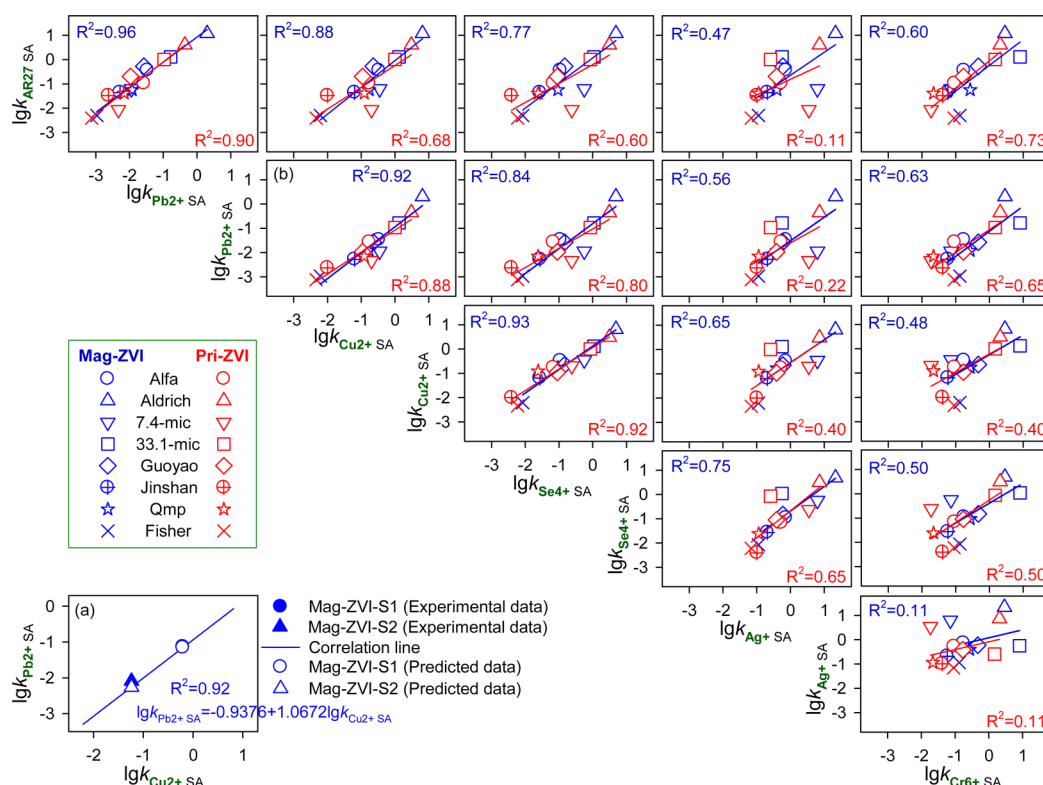
**Figure 2.** Scatter plot matrix of the specific rate constants ($\lg k_{SA}$, L m$^{-2}$ min$^{-1}$) for all combinations of contaminants removal by Pri-ZVI and Mag-ZVI. Each symbol in one plot represents one of the eight types of ZVI. Figure 2(a) shows the consistency of the experimentally determined values of $\lg k_{Pb2+SA}$ by two Mag-ZVI samples (not included in Figure 2(b)) with those predicted from the Pearson correlation illustrated in Figure 2(b).

premagnetization for enhancing the reactivity of ZVI toward pollutants treatment.

**Correlation Analysis among the Rate Constants for All Combinations of Contaminants Removal by Pri-ZVI and Mag-ZVI.** It is well recognized that a successful correlation analysis could be used to predict the data that are not available. Therefore, the correlations among $k_{obs}$ for all combinations of the contaminants and ZVI samples were performed, as shown in Figure S8. Nevertheless, the $k_{obs}$ data do not exhibit clear trend in the reactivity of ZVI toward contaminants sequestration. This phenomenon coincided with the widely held viewpoints that the raw kinetic data for contaminants removal by ZVI were highly variable.[2,3] Johnson et al.[2] unraveled that the variability in the observed degradation rates for most individual compounds by ZVI from different sources should be mainly associated with the effects of iron surface area concentration. Therefore, the specific rate constants ($k_{SA}$), yielded from the normalization of $k_{obs}$ data to the iron surface area concentration (eq 2),[2] are of great help in investigating the generality of the ZVI's reactivity and understanding the relationships between the descriptor variables for substrates sequestration by ZVI.

$$k_{SA} = -k_{obs}/\rho_a \qquad (2)$$

where $k_{SA}$ are the specific reaction rate constants (L m$^{-2}$ min$^{-1}$) of contaminant removal, and $\rho_a$ is the surface area concentration of ZVI (m$^2$ L$^{-1}$ of solution) (Table 1). The obtained $k_{SA}$ values for various contaminant-ZVI combinations are summarized in Figure S9. Due to the application of premagnetization, the median value of $k_{SA}$ increased from 0.073 to 0.211 L m$^{-2}$ min$^{-1}$ for AR27, from 0.009 to 0.019 L m$^{-2}$ min$^{-1}$ for Pb2+, from 0.148 to 0.280 L m$^{-2}$ min$^{-1}$ for Cu2+,

from 0.079 to 0.129 L m$^{-2}$ min$^{-1}$ for Se4+, from 0.321 to 0.576 L m$^{-2}$ min$^{-1}$ for Ag+ and from 0.091 to 0.222 L m$^{-2}$ min$^{-1}$ for Cr6+, respectively.

The scatter plot matrix in Figure 2 illustrates the Pearson correlations among the specific rate constants ($\lg k_{SA}$) for all combinations of contaminants removal by Pri-ZVI and Mag-ZVI, where each symbol in each plot represents one of the eight types of ZVI. Manifestly, the combinations of AR27, Pb2+, Cu2+, and Se4+ reveal linear correlations with correlation coefficients ≥0.60 and some of them are prominent with correlation coefficients ≥0.90. The strong linear correlation between $\lg k_{SA}$ of one particular contaminant removal by various Pri-ZVI or Mag-ZVI samples and $\lg k_{SA}$ of the other contaminant could be successfully employed to predict the $k_{SA}$ of one contaminant by one ZVI sample (not included in the correlation) if that of the other contaminant is available. Figure 2(a) shows the perfect consistency of the experimentally determined values of $\lg k_{Pb2+SA}$ by two Mag-ZVI samples with those predicted from $\lg k_{Cu2+SA}$ by these two Mag-ZVI samples and the correlation illustrated in Figure 2(b) (the kinetics of Pb2+ and Cu2+ removal by these two Mag-ZVI samples is shown in Figure S10). However, there are very poor correlations for several combinations of contaminants removal by Pri-ZVI and Mag-ZVI, which mainly involve Ag+ or Cr6+. The poorest correlation is Cr6+ vs Ag+ ($R^2 = 0.11$ for Pri-ZVI), and the detrimental effects of Cr6+ also exhibit in other particular correlations, for example, Cr6+ vs Se4+ ($R^2 = 0.50$ by Pri-ZVI) and Cr6+ vs Cu2+ ($R^2 = 0.40$ by Pri-ZVI), which is most likely due to the passivating effect of Cr6+ on ZVI.[9] On the other hand, the low value of rate constants ($\lg k_{SA}$) for 7.4-mic distorts the plots involving AR27 vs Ag+ ($R^2 = 0.11$ by Pri-ZVI) and Pb2+ vs Ag+ ($R^2 = 0.22$ by Pri-ZVI), but the
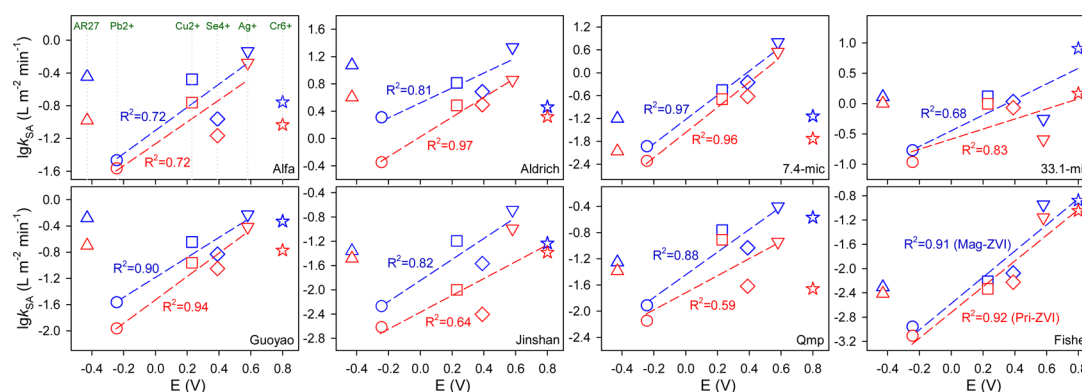
**Figure 3.** Relationship of the specific rate constants ($\lg k_{SA}$, L m$^{-2}$ min$^{-1}$) for various contaminants eliminated by Pri-ZVI and Mag-ZVI samples with the redox potentials ($E$, $V$) of the contaminants.

remaining seven points give acceptable correlations for them ($R^2 = 0.72$ for AR27 vs Ag+ by Pri-ZVI and $R^2 = 0.75$ for AR27 vs Ag+ by Pri-ZVI, respectively).

**The Influence of Contaminants' Redox Potential on the Rate Constants of Their Sequestration by Pri-ZVI and Mag-ZVI.** All of the six contaminants employed in this study were mainly removed by ZVI via reduction under acidic conditions according to the literatures.[3,5,7,39] Therefore, the relationships between the rate constants for various contaminants eliminated by Pri-ZVI or Mag-ZVI ($\lg k_{Pri\ SA}$ and $\lg k_{Mag\ SA}$) and the redox potentials of these contaminants are plotted in Figure 3 to determine the influence of the contaminants' property on the rate constants of their sequestration by ZVI. It is interesting to find that there are strong correlations between the rate constants of contaminants removal by various Pri-ZVI/Mag-ZVI samples and the redox potentials of four pollutants (i.e., Pb2+, Cu2+, Se4+, and Ag+), which should be ascribed to the fact that these four contaminants are removed via adsorption followed by reduction by Pri-ZVI/Mag-ZVI. Although Cr6+ is well-known to be removed by ZVI via reduction, the rate constants of Cr6+ removal are generally lower than those predicted by these correlations, arising from the passivating effects of Cr6+ on ZVI.[9] On the contrary, AR27 deviates from the correlation for all the cases and the rate constants of AR27 by various Pri-ZVI/Mag-ZVI samples are always greater than those predicted from its redox potential. The higher rate constants for AR27 removal by various types of ZVI may be primarily attributed to •OH radicals produced in the Fenton-like reaction under acidic conditions (pH 4.0),[40,41] which could contribute to the AR27 removal by ZVI.

Figure 3 does not show the dependence of premagnetization's influences on the contaminants' properties. Therefore, the relationship between the average rate constants (Avg $\lg k_{SA}$) by Pri-ZVI/Mag-ZVI and the redox potentials (E) of the particular contaminants is present in Figure S11. It is interesting to find that premagnetization induced similar improvement on the average removal rate constants of different contaminants by ZVI. In addition, there are very good linear relationships between the redox potentials of Pb2+, Cu2+, Se4+, and Ag+ and their average rate constants of sequestration by various Pri-ZVI samples or Mag-ZVI samples. The slopes for both lines are almost identical, indicating that the premagnetization influence is less dependent on the property of contaminants than on the property of ZVI samples.

**Correlation of the Specific Rate Constants for Various Contaminants Removal with the Intrinsic Reactivity of ZVI.** The variations of the specific rate constants of various contaminants by different types of Pri-ZVI and Mag-ZVI are plotted in Figure S12, which illustrates that the reactivity of the eight types of ZVI samples generally drops in the following order: Aldrich >33.1-mic > Guoyao > Alfa >7.4-mic > Qmp > Jinshan > Fisher. This trend had no obvious dependence on the sizes, oxide layers, and magnetic properties of these ZVI samples. Since the properties, including the size, the constituent and depth of iron oxide layer, and the impurities of ZVI samples vary greatly with their origin, very few attempts have been made to compare the reactivity of ZVI samples from different origins via a simple descriptor variable. Xie and Cwiertny[11] showed that the plots of Cr(VI) removal capacity as a function of the rate of aqueous Fe(II) production in aged nano-ZVI suspensions yielded a positive, linear relationship. Our previous study also unraveled that sequestration of Se(IV) by aged ZVI was generally accompanied by an almost linear increase in Fe(II) with the presence of WMF.[5] However, no correlation between the rate constants of a particular contaminant sequestration by different types of ZVI and the properties of these ZVI samples has been reported up to now.[3] Therefore, a suitable descriptor variable should be developed to better identify the reactivity of different ZVI samples.[21] The process of contaminants sequestration by ZVI is akin to that of ZVI corrosion and the primary corrosion product of ZVI is Fe(II). In this study, the iron surface area concentration-normalized Fe(II) release rate ($\lg k_{Fe(II)\ release\ SA}$, mg m$^{-2}$ min$^{-1}$) from Pri-ZVI or Mag-ZVI at pH 4.0 buffered with NaAc-HAc open to the air within 120 min is proposed to stand for the intrinsic reactivity of ZVI because the oxidation of Fe(II) by oxygen in air under this condition is very slow. It should be addressed that the presence of contaminant may disturb the analysis of Fe(II) released from ZVI and affect the rate of Fe(II) released from ZVI and thus the intrinsic reactivity of ZVI was determined without the presence of contaminant. The intrinsic reactivity, which is an invariable and independent of other reaction conditions,[21] for example, solution chemistry, the properties of the contaminants, as well as other mutual effects,[42,43] could be employed to compare the reactivity of multiple ZVI samples under identical conditions.

Therefore, the kinetics of Fe(II) release from Mag-ZVI and Pri-ZVI at pH 4.0 buffered with NaAc-HAc open to the air were determined and the major data sets of the Fe(II) release kinetics were simulated well with zero-order rate law, as shown
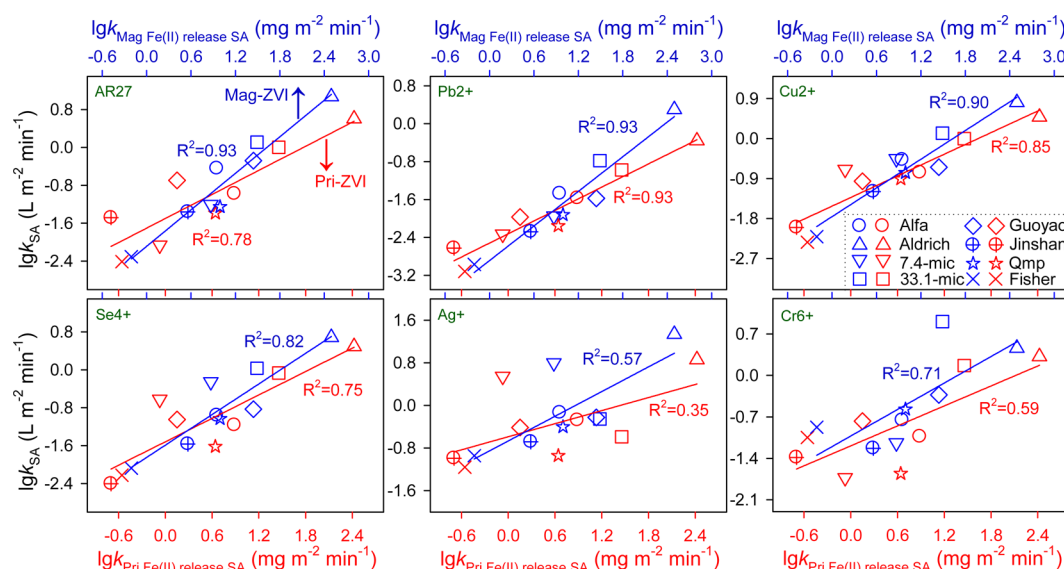
**Figure 4.** Pearson correlation of the specific rate constants ($\lg k_{SA}$, L m$^{-2}$ min$^{-1}$) of various contaminants removal by Pri-ZVI or Mag-ZVI with the intrinsic reactivity of these ZVI samples ($\lg k_{Pri/Mag\ Fe(II)\ release\ SA}$, mg m$^{-2}$ min$^{-1}$).

in Figure S13. Evidently, the three Pri-ZVI samples (Alfa, Aldrich, and 33.1-mic) containing the least surface iron oxides, as revealed by the Raman spectra in Figure S3, released Fe(II) with much greater rates than the other five Pri-ZVI samples. Moreover, these three Pri-ZVI samples could remove various contaminants with relatively greater constants compared to the other Pri-ZVI samples, implying that the amount of iron oxides on ZVI surface is crucial for the reactivity of ZVI. The intrinsic reactivity of all Pri-ZVI and Mag-ZVI samples calculated from Figure S13 is summarized in Table 1, which reveals that premagnetization improved the intrinsic reactivity of all Pri-ZVI samples employed in this study but the premagnetization-induced enhancement varied largely for different Pri-ZVI samples.

It was expected that the rate constants of one specific contaminant removal by different types of ZVI under identical reaction conditions were positively related to the intrinsic reactivity of these ZVI samples. Therefore, the Pearson correlations of the rate constants ($\lg k_{SA}$) for AR27, Pb2+, Cu2+, Se4+, Ag+, and Cr6+ removal by eight types of Pri-ZVI and Mag-ZVI with the intrinsic reactivity of these ZVI samples ($\lg k_{Pri/Mag\ Fe(II)\ release\ SA}$) are plotted in Figure 4. The poor correlation between the rate constants of Ag+ removal and the intrinsic reactivity of various ZVI samples mainly stemmed from the unexpected high reactivity of the 7.4-mic ZVI sample toward Ag+ removal. Excluding the data of Ag+ removal by the pristine or the premagnetized 7.4-mic ZVI sample, the correlation coefficients of the rate constants ($\lg k_{SA}$) for Ag+ removal by seven types of Pri-ZVI and Mag-ZVI with the intrinsic reactivity of these ZVI samples ($\lg k_{Pri/Mag\ Fe(II)\ release\ SA}$) were improved to 0.71 and 0.83, respectively. Generally, there are strong positive correlations between the removal rate constants of contaminants (especially for AR27, Pb2+, Cu2+, Se4+) by eight types of Pri-ZVI/Mag-ZVI and the intrinsic reactivity of these Pri-ZVI/Mag-ZVI samples with correlation coefficients ≥0.75. In addition, the correlations between the removal rate constants of Cr6+ and the intrinsic reactivity of these Pri-ZVI or Mag-ZVI samples were not very desirable, which may be associated with the passivating effect of Cr6+. However, as shown in Figure S14, the average removal

rates of various contaminants by different ZVI samples are closely related to their specific Fe(II) release rate constants and premagnetization resulted in an increase in the slope of the correlation, indicating that premagnetization enhanced the reductive removal of these contaminants because the reductive removal contaminants was accompanied by a release of Fe(II).[8,17]

It should be addressed that all the variables used in the correlation analysis are normally distributed (Asymp. (2-tailed) > 0.05, i.e., $P > 0.05$) (Table S3), suggesting that the Pearson correlation was preferable to the Spearman correlation analysis. The disadvantage of Spearman correlation is that there is a loss of information when the data are converted to ranks, thus, the Spearman correlation is less powerful than the Pearson correlation.[44] Our results did show that the statistical significances of the Spearman correlation were poorer than those of the Pearson correlation for most cases, as shown in Table S4. Consequently, the Pearson correlation was employed to analyze the complex data set in this study.

The positive correlation between specific Fe(II) release rate constants and the removal rate constants of a specific contaminant could be employed to predict the removal rate constant for this contaminant by a ZVI sample that was not included in the original data set, once the intrinsic reactivity of this ZVI sample was known. As illustrated in Figure S15, the $k_{SA}$ of Cu2+ removal by two Mag-ZVI samples could be well predicted by the intrinsic reactivity of these two Mag-ZVI samples and the corresponding regression line shown in Figure 4.

The intrinsic reactivity of various ZVI samples determined at pH 4.0 is also expected to be strongly correlated with the rate constants of contaminants removal at other pH levels. Therefore, the kinetics of Cu2+ removal by eight Mag-ZVI samples was determined at pH 5.0 (Figure S16). It was found that there was a strong positive linear relationship ($R^2 = 0.88$) between the rate constants of Cu2+ removal at pH 5.0 and the intrinsic reactivity of these Mag-ZVI samples (Figure S17). Moreover, it was found that the Fe(II) release rates of various Mag-ZVI samples under anoxic conditions ($\lg k''_{Mag\ Fe(II)\ release\ SA}$ (Purged with nitrogen, mg m$^{-2}$ min$^{-1}$))

correlated well with the intrinsic reactivity of these Mag-ZVI samples, as shown in Figures S18 and S19. It implied that the intrinsic reactivity of ZVI samples determined open to the air could be employed to evaluate their reactivity under anoxic conditions when they are used in permeable reactive barrier. Consequently, to evaluate the relative reactivity of various ZVI samples, it was not necessary to determine the sizes, constituents of passive layer, and the impurities of these ZVI samples but to determine the Fe(II) release rates of these ZVI samples under well controlled conditions and the specific surface area.

**Environmental Implications.** The specific Fe(II) release rate was proposed for the first time to stand for the intrinsic reactivity of ZVI sample. With this parameter, the relative reactivity of different ZVI samples toward a particular contaminant can be evaluated easily just by determining the rate constants of Fe(II) under well-controlled conditions and the specific surface area of these ZVI samples. The efficiency of contaminant removal by ZVI is heavily influenced by pH, the properties of contaminant, the concentration of dissolved oxygen, and other operation conditions, whereas the intrinsic reactivity of one ZVI sample is an invariable.

The results of this manuscript showed that all Mag-ZVI samples had higher intrinsic reactivity than their counterparts without premagnetization. Consequently, premagnetization could improve the sequestration of various contaminants by ZVI from different origins. There are strong correlations between the intrinsic reactivity of various ZVI samples and the removal rate constants of a specific contaminant by these ZVI samples not only at pH 4.0 when the intrinsic reactivity is determined but also at other pH levels. These correlations can be employed to predict the removal rate constant of this contaminant by a ZVI sample that was not included in the original data set once the intrinsic reactivity of the ZVI sample was known. It should be specified that this study only investigated the enhancing effect of premagnetization on the initial reactivity of various ZVI samples. The influence of premagnetization on the long-term reactivity of various ZVI samples is under investigation in our lab considering the application of ZVI in permeable reactive walls.

### ■ ASSOCIATED CONTENT

#### Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b04215.

SEM images, particle size distribution, Raman spectra and magnetic hysteresis loops of the pristine ZVI samples, kinetics of AR27, Pb2+, Cu2+, Se4+, Ag+, and Cr6+ removal by Pri-ZVI/Mag-ZVI, release of dissolved Fe(II) during Pb2+, Cu2+, Se4+, and Ag+ removal by Pri-ZVI/Mag-ZVI samples, bubble plot of the promotion factors ($f = k_{Mag}/k_{Pri}$) for contaminants sequestration due to premagnetization, scatter plot matrix of rate constants ($k_{obs}$, min$^{-1}$) for all combinations of contaminants removal by Pri-ZVI and Mag-ZVI samples, rate constants ($k_{SA}$, L m$^{-2}$ min$^{-1}$) of Cr6+, Ag+, Se4+, Cu2+, Pb2+, and AR27 sequestrated by Pri-ZVI/Mag-ZVI, kinetics of Pb2+ and Cu2+ removal by Mag-ZVI-S1/Mag-ZVI-S2, the relationship between the average rate constant (Avg log$k_{SA}$, L m$^{-2}$ min$^{-1}$) of each contaminant by all types of ZVI samples and the redox potentials ($E$, $V$) of these contaminants, rate constants

($\lg k_{SA}$, L m$^{-2}$ min$^{-1}$) for disappearance of Cr6+, Ag+, Se4+, Cu2+, Pb2+, and AR27 by Pri-ZVI/Mag-ZVI, the kinetics of Fe(II) release from the Pri-ZVI/Mag-ZVI samples employed in this study without presence of contaminants, the correlation of the average rate constants (Avg $\lg k_{SA}$, L m$^{-2}$ min$^{-1}$) for all combinations of contaminants with the Fe(II) release rates ($\lg k_{Fe(II)\ release\ SA}$, mg m$^{-2}$ min$^{-1}$) of the Pri-ZVI and Mag-ZVI from different origins, the consistency of the experimentally determined values of $\lg k_{Cu2+SA}$ by Mag-ZVI-S1/Mag-ZVI-S2 with those predicted from the correlation illustrated in Figure 4, kinetics of Cu2+ removal by various Mag-ZVI samples at pH 5.0, the correlation of the specific rate constants ($\lg k_{Mag\ SA}$, L m$^{-2}$ min$^{-1}$) for Cu2+ removal by Mag-ZVI (pH 5.0) with the intrinsic reactivity of Mag-ZVI samples ($\lg k_{Mag\ Fe(II)\ release\ SA}$, mg m$^{-2}$ min$^{-1}$), the kinetics of Fe(II) release from the Mag-ZVI samples under nitrogen-purging conditions without the presence of contaminants, the correlation of the Fe(II) release rates of various Mag-ZVI samples under anoxic conditions (purged with nitrogen, $\lg k''_{Mag\ Fe(II)\ release\ SA}$, mg m$^{-2}$ min$^{-1}$) with the intrinsic reactivity (open to the air, $\lg k_{Mag\ Fe(II)\ release\ SA}$, mg m$^{-2}$ min$^{-1}$) of these Mag-ZVI samples, properties of contaminants, the mean observed rate constants ($k_{obs}$, min$^{-1}$) for contaminants sequestration by Pri-ZVI and Mag-ZVI, statistics of the normal distribution, and the statistical significances derived from the Pearson correlation and Spearman correlation (PDF)

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#### Notes
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### ■ ACKNOWLEDGMENTS

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