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USE OF ZERO-VALENT IRON FOR WASTEWATER TREATMENT

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ABSTRACT

Nowadays many water resources are polluted by anthropogenic sources including household and agricultural waste and industrial processes. Public concern over the environmental impact of wastewater pollution has increased. Several conventional wastewater treatment techniques, i.e. chemical coagulation, adsorption, activated sludge, have been applied to remove the pollution, however there are still some limitations, especially that of high operation costs. The use of zero-valent iron as a reductive medium is receiving increased interest due to its low operation and maintenance costs. In addition, it is easy-to-obtain, with good effectiveness and ability for degrading contaminants. This paper reviews the use of zero-valent iron to remove contaminants from wastewater such as halogenated hydrocarbon compounds, heavy metals, dyes, pesticides, and herbicides, which represent the main pollutants in wastewater.

KEYWORDS: Wastewater treatment, Zero-valent iron

1. INTRODUCTION

Water pollution is one of the largest environment problems in several countries. It mainly arises from wastewater released from household, industrial and agricultural processes. These effluents typically contain high concentrations of organic and inorganic chemicals such as hydrocarbon solvents, heavy metals, pesticides, dyes and so on. The toxicity, persistency and concentration of the contaminants result in serious environmental, public health and economic impacts. Consequently, treatment of wastewater before release into the environment is required. There are several wastewater treatment techniques including physical, chemical or biological processes i.e. coagluation, flocculation, adsorption, reverse osmosis, activated sludge and so on. However, there are some disadvantages especially high operation and maintenance costs [1]. A use of zero-valent iron (Fe^0) as reactive medium for wastewater treatment is one of the most promising techniques because the iron metal is of low-cost, is easy-to-obtain, and has good effectiveness and ability of degrading contaminants. In addition, iron waste particles from industrial filings can be used as a zero-valent iron [2-3]. Reactive barriers containing iron metals are currently being developed for *in situ* treatment technology [4]. As zero-valent iron is a strong reducer, it has been used to remove several contaminants as shown in table 1 [5].

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Table 1 Contaminants treated by zero-valent iron [5]

Organic compounds		**Inorganic compounds**	
Methanes	Tetrachloromethane	**Trace metals**	Arsenic
	Trichloromethane		Cadmium
	Dichloromethane		Chromium
Ethanes	Hexachloroethane		Cobalt
	1,1,1-trichloroethane		Copper
	1,1,2-trichloroethane		Lead
	1,1-dichloroethane		Manganese
	1,2-dibromoethane		Nickel
Ethenes	Tetrachloroethene		Selenium
	Trichloroethene		Uranium
	cis-1,2-dichloroethene		Zinc
	trans-1,2-dichloroethene	**Anion contaminants**	Nitrate
	1,1-dichloroethene		Phosphate
	Vinyl chloride		Sulfate
Propanes	1,2,3-trichloropropane		
	1,2-dichloropropane		
Aromatics	Benzene		
	Toluene		
	Ethylbenzene		
Others	Hexachlorobutadiene		
	Freon 113		
	n-nitrosodimethylamine		

2. DEGRADATION OF POLLUTANTS

The use of zero-valent iron for wastewater treatment has been increasingly studied. However, the exact mechanism of degradation of contaminants in the presence of iron is not fully understood. There are many works proposing that the degradation mechanism comprises of heterogeneous reactions. The reactions occur when the reactant molecules reach the iron solid surface. They then associate with the surface at sites that may be either reactive or non-reactive. Competition can also occur between the reactant solute of interest and other solutes for the available sites [6]. The reactive sites refer to those where the breaking of bonds in the reactant solute molecule take place (i.e. chemical reaction) whilst non-reactive sites are those where only sorption interactions occur and the solute molecule remains intact.

2.1 Dehalogenation of halogenated organic compounds

Zero-valent iron has been used to rapidly dehalogenate a wide range of halogenated organic compounds [7-21]. The degradation hypothesis of halogenated compounds by iron is better accepted as there is a reductive dehalogenation of the contaminant coupled with corrosion of the iron. With a standard reduction potential (E_h°) of -0.44 V, Zero-valent iron (Fe^0) primarily acts as a reducing agent. The iron is oxidized (electron donor) (equation 1) whilst alkyl halides (RX) are reduced (electron acceptor) (equation 2). Because the estimated standard reduction potentials of the dehalogenation half-reaction of various alkyl halides range from +0.5 to +1.25 V at pH 7 [22], the net reaction is thermodynamically very favorable under most conditions (equation 3).

$$Fe^0 \longrightarrow Fe^{2+} + 2e^- \tag{1}$$

$$RX + 2e^- + H^+ \longrightarrow RH + X^- \tag{2}$$

$$Fe^0 + RX + H^+ \longrightarrow Fe^{2+} + RH + X^- \quad (3)$$

For example, groundwater contaminated with chlorinated solvents such as trichloromethane (TCM), trichloroethylene (TCE), perchloroethylene (PCE) is treated using iron barriers. The preferred electron acceptor is typically dissolved oxygen under aerobic conditions (E_h° +1.23 V). This acceptor can compete with chlorinated hydrocarbons that have similar oxidizing potentials to oxygen (O_2). Aerobic groundwater enters the iron fillings wall, and causes the oxidation of metallic iron (Fe^0) to ferrous iron (Fe^{2+}) with the subsequent release of two electrons (equation 1). Chlorinated solvents also react as electron acceptors, resulting in dechlorination and release of a chloride ion (equation 2). The reaction takes place in several steps resulting in reducing halogenated organic compounds via intermediates, to non-toxic compounds such as ethylene, ethane, and acetylene [9-11, 14-16, 20]. Intermediate compounds like vinyl chloride, which has a higher toxicity than the parent, are not formed in high concentrations [21].

Zero-valent iron also reacts with water producing hydrogen gas and hydroxide ions resulting in an increase in the pH of the water (equation 4). Hydrogen gas can also react with alkyl halides (equation 5).

$$Fe^0 + 2H_2O \longrightarrow Fe^{2+} + 2OH^- + H_2 \quad (4)$$

$$RCl + H_2 \longrightarrow RH + HCl \quad (5)$$

The bulk dehalogenation reaction is usually described by first-order kinetics [6, 12, 18-19]. The lower the degree of chlorination, the slower the rate of dechlorination reaction [8, 17]. Batch and column testings have also indicated highly variable degradation rates due to operating conditions and experimental factors such as pH, metal surface area, concentration of pollutants, and mixing rate. Some authors suggested a combination of zero and first-order equation with respect to the concentration of halogenated hydrocarbon in water [18]. Since the reaction is heterogeneous, its rate is also proportional to a specific surface area of the iron used [23]. Therefore the adsorption, desorption or diffusion of reactants and chemical reaction itself can limit the processes. Activation energy of the reaction varies from 30 to 80 kJ mol^{-1} according to the particular chlorinated hydrocarbon [9, 19]. Several limitations of this technique, including the accumulation of chlorinated by-products and the decrease in the activity of iron over the time, have been reported [10, 23-25]. Improved methods that involve physical and chemical processes include (1) increasing the surface area of iron by reducing its particle size to enhance the reactivity [23]; (2) combining ultrasound and iron to accelerate dechlorination reaction and reduce the forming of oxide layers on the surface of the iron by continuous cleaning through acoustic cavitation [26]; and (3) depositing a second metal as a catalyst onto the surface of the iron [24, 27-33].

2.2 Removal of Heavy Metals

Zero-valent iron has been widely studied for removal of heavy metals such as chromium, arsenic [3, 34-40]. The degradation mechanisms are based on transformation from toxic to non-toxic forms or adsorption on the iron surface depending on the type of heavy metals.

The removal of chromium by zero-valent iron is based on transformation from toxic to non-toxic forms. Hexavalent chromium (Cr(VI)), which is a strong oxidant, a potential carcinogen and more mobile in soils and aquifers, is transformed to trivalent chromium (Cr(III)), which is less hazardous and less water soluble and associated with solids [3-4]. The reduction rate of Cr(VI) by Fe(0) produces ferric ion (Fe(III)) and chromium ion (Cr(III)) (equation 6). Chromium (III) may be removed through the precipitation or co-precipitation in terms of mixed Fe(III) and Cr(III) hydroxide as shown in equation 7 [34] or equation 8.

$$Cr^{6+} + Fe^0 \longrightarrow Cr^{3+} + Fe^{3+} \quad (6)$$

$$(1\text{-}x)Fe^{3+} + (x)Cr^{3+} + 3H_2O \longrightarrow (Cr_xFe_{(1-x)})(OH)_3\ (s) + 3H^+ \quad (7)$$

$$(1\text{-}x)Fe^{3+} + (x)Cr^{3+} + 2H_2O \longrightarrow Fe_{(1-x)}Cr_xOOH\ (s) + 3H^+ \quad (8)$$

The reduction rate of Cr(VI) by Fe(0) is accelerated when mineral surfaces such as goethite (α-FeOOH) and aluminium oxide (γ-Al_2O_3) are present and the pH of the solution is low [35-36]. This reaction rate is quite fast. Therefore the oxidation of the Fe(0) and Fe(II) is not only dependant on type of contaminants but also operating conditions [35].

The removal of arsenic by zero-valent iron does not involve reduction to metallic form [41], it only involves surface complexation. Iron hydroxide (active phase) has to be formed on the surface of the particles before arsenic can be bound to this material under oxidizing conditions [41]. There are several works supporting this hypothesis [37-40]. The removal efficiency is related to the surface area or the type of iron used and improves over time, possibly due to pitting of the iron surface and increased surface area for sorption due to iron corrosion and ferrous iron adsorption or precipitation [37-40]. Therefore, both As (III) and As (V) can be removed from aqueous using zero-valent iron [37].

2.3 Decolorization of Dye Compounds

Fe^0 has recently been studied to decolorize textile wastewater [42-45]. The destruction of the azo bond (N=N) in the chromophore of azo dyes leads to decolorization of the dye solutions as shown in figure 1. The iron particle is oxidized while the dye molecule is reduced. The dye molecule receives electrons from the iron and combines with H^+ from an acid to form the transitional product. This product gains electrons and combines with H^+ again, forming the terminal products [43]. Additionally, in the presence of Fe^0, aromatic azo compounds are susceptible to reduction to produce aromatic amines which are easily degraded by microorganisms [45]. Several experiments [46-47] also confirm that under reactive conditions, azo dyes are decomposed through N-N cleavage with the formation of aromatic amines such as aniline. As aromatic amines are toxic, a combination treatment of zero-valent technique with other wastewater treatment technologies may be required. Batch kinetic studies show that the decolorization rate follows first order equation [45]. It was found that only small amount of dyes was adsorbed on the iron surface [45] and sorption data of dyes on the iron surfaces fitted with Langmuir isotherm [43].

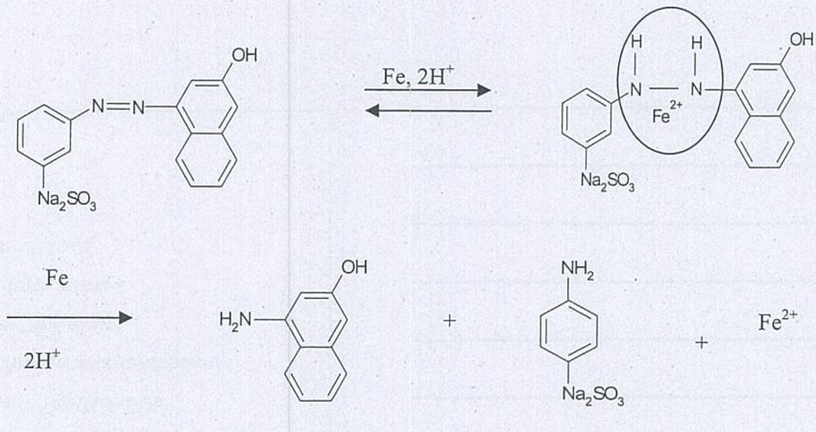

Figure 1 Degradation mechanism of Acid Orange II in Fe^0-H_2O system [43]

2.4 Degradation of Herbicides and Pesticides

Since many herbicides and pesticides contain halogens, they will be subject to degradation by dehalogenation using zero-valent iron [46-50]. Pesticides containing halogenated compounds such as metolachlor, alachlor, atrazine, pendimethalin, chlorpyrifos can be reduced when coupled to the corrosion of iron metal, with Fe(0) and Fe(II) serving as reductants [48-49, 51-52]. The degradation rate of pesticides is enhanced by adding $Al_2(SO_4)_3$ and CH_3COOH to the Fe^0 [48-52]. This may be due to the resulting pH and soil solution composition during corrosion of Fe^0 [49]. The sustained mildly acidic to near neutral pH of treatment containing $Al_2(SO_4)_3$ may enhance the effectiveness of Fe^0 by slowing oxidation and passivation (deactivation by Fe(III) oxide formation) while maintaining reactive Fe(II) on the oxide surface. The presence of Fe^{2+}, Fe^{3+} or Al^{3+} during Fe^0 corrosion promotes pesticide destruction [51]. Addition of $Al_2(SO_4)_3$ also provide sulfate, which sustains higher rates of iron corrosion by dissolving the oxide film that coats the surface during oxidation [52]. It was found that the dicamba (herbicide) removal was primarily through adsorption [53]; however, when the Fe^0 was augmented with Al(III) or Fe(III) salts, dicamba was dechlorinated to an unidentified product [53].

3. USE OF ZERO-VALENT IRON AS DEGRADATION BARRIERS

General degradation barriers are designed to break down or degrade contaminants in groundwater into harmless products by employing enhanced biological degradation or chemical destruction mechanisms. Barriers filling with zero-valent iron have been widely used for the degradation of chlorinated solvents such as TCE and PCE.

Experimentally determined degradation rate constants for zero-valent iron treatment walls are typically obtained by laboratory batch testing in which the rate constant is calculated from the slope of a semilog plot of the normalized concentration (C_0/C_t) versus time, where C_0 is the initial concentration and C_t is the concentration at time t. These estimated rate constants are typically decreased by 50 percent to adjust for subsurface temperatures in groundwater, which are lower than room temperature.

The amount of iron used is the most significant cost factor in the construction of the treatment walls. The mass of iron required to decrease chemical concentrations to acceptable levels can be calculated from equation 9 as follows:

$$\mathrm{W/A} = (\mu n/k_i) \ln (C_0/C) \tag{9}$$

Where W = weight of iron required
A = cross-sectional area of the plume
μ = groundwater flow velocity
n = aquifer porosity
k_i = chemical-specific degradation rate constant
C_0 = upgradient contaminant concentration
C = remedial objective down-gradient of the treatment wall

The first-order rate constant k_i can be calculated from the surface-area-specific rate parameter k_{sa} and the specific surface area for granular iron (typically 1.0 m^2/g). Surface-area-specific rate constant for selected organic chemicals with zero-valent iron is shown in table 2 [54].

Equation 9 is often modified to include a safety factor F, which accounts for uncertainties in site conditions. A recommended safety factor of 3.5 has been proposed [55] and incorporated in equation 10.

$$\mathrm{W/A} = F(\mu n/k_i) \ln (C_0/C) \tag{10}$$

There are several sites using zero-valent iron as treatment walls as shown in table 3 [5].

Table 2 Surface-area-specific rate constant for selected organic chemicals with zero-valent iron [54]

Chemical	k_{sa}, L/(m^2 x h)*
Tetrachloromethane (PCM)	$1.2 \pm 1.5 \times 10^{-4}$
Trichloromethane (TCM)	$9.2 \pm 7.3 \times 10^{-4}$
Tribromomethane (TBM)	1.7×10^{-2}
Hexachloroethane (HCA)	$3.1 \pm 3.3 \times 10^{-2}$
1,1,2,2-tetrachloroethane (1,1,2,2-PCA)	1.3×10^{-2}
1,1,1,2-tetrachloroethane (1,1,1,2-PCA)	1.4×10^{-2}
1,1,1-trichloroethane (1,1,1-TCA)	1.1×10^{-2}
1,2,3-trichloropropane (1,2,3-TCP)	$6.1 \pm 4.7 \times 10^{-6}$
Tetrachloroethene (PCE)	$2.1 \pm 2.7 \times 10^{-3}$
Trichloroethene (TCE)	$3.9 \pm 3.6 \times 10^{-4}$
1,1-dichloroethene (1,1-DCE)	$6.4 \pm 5.5 \times 10^{-5}$
trans-1,2-dichloroethene (t-1,2-DCE)	$1.2 \pm 0.4 \times 10^{-4}$
cis-1,2-dichloroethene (c-1,2-DCE)	$4.1 \pm 1.7 \times 10^{-6}$
Vinyl chloride (VC)	$5.0 \pm 1.5 \times 10^{-5}$

*L = barrier thickness

Table 3 Summary of zero-valent iron used in selected treatment walls [5]

Site	Capture area (ft^2)	W/A (lb/ft^2)	Iron (tons)
Coffeyville, Kansas	7,500	19	71
Belfast, North Ireland	650	46	15
Denver, Colorado	11,700	99	580
Elizabeth City, North California	2,900	210	300
Mountainview, California	660	270	90
Lowry AFB, Colorado	270	330	45
Upstate New York	270	380	45
Moffett AFB, California	475	400	96
Somersworth, New Hampshire	250	520	65
Sunnyvale, California	520	850	220

4. CONCLUSIONS

Zero-valent iron can be used to remove wastewater pollutants such as halogenated hydrocarbon compounds, heavy metals, dyes, pesticides, and herbicides under reduction reactions or sorption process. Due to its fast reaction, low cost and ease-to-obtain, the zero-valent iron has been gaining interest for removal of pollutants in wastewater. Although soluble iron, which is a by-product from the reaction, is not toxic, other intermediate products resulting from degradation should be determined. Types of intermediate compounds are dependent on their substances. Some substances are converted from toxic into non-toxic forms such as ethylene, ethane, and acetylene reduced from halogenated organic compounds whilst some intermediate compounds are toxic such as aniline degraded from azo dyes. To reach the wastewater emission standard, a combination of zero-valent iron technique with other wastewater treatment technologies may be required.

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