Degradation of 17β-estradiol by Zero Valent Iron

Clayton J Clark II[1*], Yvette E Pearson[2] and Leslie M Pipkin[3]

[1]Department of Civil and Environmental Engineering Florida A&M University Tallahassee, FL 32307, USA

[2]George R. Brown School of Engineering Rice University Houston TX 77407, USA

[3]Department of Civil and Environmental Engineering FAMU/FSU College of Engineering Tallahassee, FL 32310, USA

*Corresponding author: Clayton J Clark II, Ph.D., P.E., Department of Civil and Environmental Engineering Florida A&M University FAMU-FSU College of Engineering, Rm A126 Tallahassee, Florida 32310, USA, Tel: (850) 410-6122; Fax: (850) 410-6142: **E-mail:** clayton.clarkii@famu.edu

Abstract

Endocrine disrupting compounds (EDCs) in aquatic environments are often found as a result of industrial, agricultural, and sewage runoff from wastewater treatment plants. One prevalent EDC, 17β-estradiol, is of great environmental concern due to its only partial removal by wastewater treatment plants. The purpose of this study was to: first, explore the potential degradation of 17β-estradiol in water when contacted with zero valent iron (ZVI); next, if effective, quantify the degradation kinetics of 17β-estradiol in water when contacted by ZVI; and lastly, determine if treatment of 17β-estradiol by ZVI can be related to the amount of ZVI present. The research found that ZVI effectively degraded 17β-estradiol in water and displayed a pseudo-1st order degradation rate. The degradation rate constants were 0.523 hr-1, 0.425 hr-1, and 0.406 hr-1 for volume of solution-to-mass of iron ratios of 2:1, 4:1, and 8:1, respectively. Also, half-lives for the varying ratios were calculated as 1.33 hr, 1.63 hr, and 1.71 hr for the volume of solution-to- mass of iron ratios of 2:1, 4:1, and 8:1, respectively. Results also showed that >99% of the initial 2 ppm concentration of 17β-estradiol mass in water degraded in the presence of ZVI. Increase in ZVI mass relative to aqueous volume resulted in higher degradation rates and lower half-lives for 17β-estradiol. These results compared favorably with ZVI treatment of other contaminants in water provided in the literature, including other EDCs, pesticides, and chlorinated organics. After degradation of 99% of the mass of 17β-estradiol, no appreciable oxide formation was noted by SEM analysis of the ZVI. Overall, ZVI has been shown to effectively degrade 17β-estradiol in aqueous environments with increased effectiveness with greater mass of the substrate included. The optimization of this treatment process can improve cost effectiveness, cost efficiency, and overall sustainability in remediating harmful and EDCs from water systems.

Keywords: 17β-estradiol; Zero-valent iron; Endocrine disrupting compound; Degradation

Introduction

Theoretical Background

A broad range of anthropogenic chemicals being released into the natural environment can have undesirable impacts on aquatic ecosystems and are suspected to have negative effects on humans. One group of major concern is those known as endocrine disrupting chemicals (EDCs). EDCs have been defined as exogenous agents that interfere with the production, release, transport, metabolism, binding action, or elimination of natural hormones in the body. These hormones are responsible for the maintenance of homeostasis and the regulation of developmental processes [1-3]. Since classification as an EDC is not based upon chemical nature, but on biological effect, a wide variety of pollutants can be collectively referred to as EDCs, including pesticides, plasticizers, detergents, synthetic and natural hormones, human and veterinary pharmaceuticals, and personal care products [4,5].

EDCs are released into aquatic environments as a result of industrial, agricultural, and, despite plant treatment processes, sewage runoff from wastewater treatment plants. EDCs such as estrogens have been found in sewage or wastewater treatment effluents at concentration in the nanogram per liter to microgram per liter range, which indicates that they are only partially, removed with existing treatment processes [6]. Both natural and synthetic estrogens are often the main substance responsible for estrogenic activity found in domestic sewage [7]. A major estrogenic EDC of environmental concern in natural soil and water systems is 17β-estradiol. The widespread use of 17β-estradiol is becoming a more prominent and has led to greater research to determine the effects of this compound on the environment and humans. Excreted daily by humans in domestic sewage, 17β-estradiol is only partially removed by domestic wastewater treatment plants, and has been found in increasing amounts in surface and ground waters down gradient of these treatment facilities.

17β-Estradiol

17β-Estradiol (CAS 50-28-2) is the household name for (17β)-estra-1,3,5(10)-triene-3,17- diol (Figure 1 and Table 1). The hormone 17β-estradiol is both naturally occurring and a synthesized hormone that can be found in the environment. In its natural state, 17β-estradiol is an estrogen that is produced by human glands, mainly by ovaries and testes, and is excreted within urine and feces [8,9]. 17β-estradiol was first
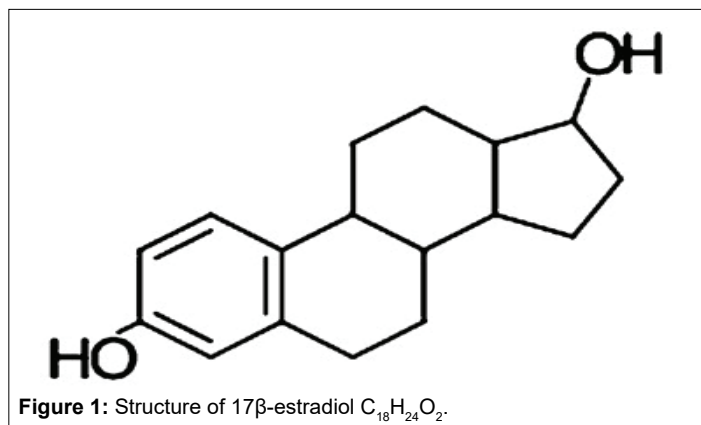

**Figure 1:** Structure of 17β-estradiol $C_{18}H_{24}O_2$.

Table 1: Chemical Properties of 17β-Estradiol

17β-Estradiol Chemical Properties	
Chemical names	(17β)-estra-1,3,5(10)-triene-3,17-diol
Molecular Formula	$C_{18}H_{24}O_2$
Molar mass	272.39 g/mol
CAS number	50-28-2
Appearance	White crystalline powder
Melting point	176-180°C
Solubility in water	3.9 mg/L Li et al. [9]
log Kow	1.3×10^{-8} Li et al. [9]

synthesized by Hans HerloffInhoffen and Walter Hohlweg in 1938 [10]. In its synthesized form, this estrogen compound is an endocrine disrupter that can disturb the estrogenic characters of animals in the environment. The 17β-estradiol hormone is being used worldwide for many different applications. It is the most commonly used oral bio-active estrogen, used in practically all modern forms of oral contraceptive pills [11]. It is also one of the most widely used substances for estrogen enhancement in livestock and is therefore found in those related agricultural soils [12,13]. Additional sources of 17β-estradiol include septic drain fields, sewage, irrigation with reclaimed water, leached pesticide and leachate from landfills and applied biosolids [14,15]. Therefore, with these multiple sources, 17β-estradiol has been found to be continuously discharged into receiving water bodies [16]. This has resulted in it, as well as a number of other EDCs, being found to reach and travel in groundwater and even re-enter drinking water supply wells [17].

Zero Valent iron treatment

Unlike other potential treatment processes for 17β-estradiol in water, the passive nature of zero valent iron in aqueous environments requires no additional power input, supplementary chemicals, or advanced equipment. Since the Gillham and O'Hannesin study [18], multiple researchers have shown ZVI to be effective in oxidizing chemical constituents eliminating and degrading them from contaminated water sources [19-23]. These investigations examined the degradation of contaminants including chlorinated ethylene, chlorinated acetylene, perchloroethylene (PCE), arsenic, toxaphene, and some complex chlorinated non-aqueous phase liquids (NAPL). Gillham and O'Hannesin's [18] research concluded that the degradation process is abiotic and electrochemical in nature. During the process there is a simultaneous occurrence of two reactions using the zero valent elemental iron: oxidation of iron by water and reduction of organic compounds in water with Fe^0 serving as the source of electrons. The proposed reactions for ZVI oxidation of contaminants in water presented by Gillham and O'Hannesin [18] include:

$$2Fe^0 \rightarrow 2Fe^{2+} + 4e^- \qquad (1)$$

$$3H_2O \rightarrow 3H^+ + 3OH^- \qquad (2)$$

$$2H^+ + 2e^- \rightarrow H_2 \qquad (3)$$
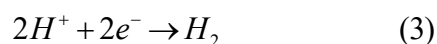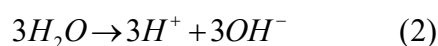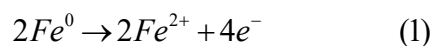
These reactions provide a reducing environment that tends to keep the contaminant of concern thermodynamically unstable, causing degradation to occur.

Overall Purpose

Drinking water quality is a major priority for mankind. As concerns grow with respect to EDCs leaching into drinking water sources, many researchers are looking to find ways to remove these harmful chemicals from the environment. Though multiple studies have focused on specific technologies that would eliminate 17β-estradiol and other EDCs during

wastewater treatment and water treatment processes, there have been no work related to ZVI degradation of this EDC in water.

The purpose of this study was to explore the potential degradation of when contacted with zero valent iron (ZVI). The research seeks to, first; determine if ZVI can effectively treat 17β-estradiol in water. Secondly, if effective, the research seeks to quantify the degradation kinetics of 17β-estradiol in water when contacted by ZVI. Lastly, it the research would seek to determine if treatment of 17β-estradiol by ZVI can be related to amount of iron substrate present. Each of these objectives would provide novel information related to treatment of contaminated water sources.

Materials and Methods

Experimental methodology

The 17β-estradiol degradation experiments were performed in sealed individual glass vials analyzed at various time intervals over a one-week time period. These individual vials acted as batch reactors and were used to evaluate the degradation kinetics of 17β-estradiol in aqueous solutions in contact with zero-valent iron substrate. Each sample was prepared in 5 mL glass vials fitted with a Teflon-lined septa screw-top cap. Amber glass was utilized to limit photodegradation that might occur during experimentation to ensure that all degradation would occur by contact with ZVI. Initially, the empty vials were weighed and a mass of 1.25 g of ZVI was added to each vial. The vials were then filled with a ~2 ppm 17β-estradiol aqueous solution, allowing no headspace, and re-weighed. No headspace would also maintain that all 17β-estradiol degraded would occur within the aqueous phase and not by volatilization. This would establish a 4:1 volume of solution to mass of ZVI ratio. This methodology has been successfully utilized by several researchers in measuring the effectiveness of ZVI degradation of contaminants in water [18,20,22,24].

In addition to the 4:1 ratio, two other ratios were examined to determine the effect of ZVI amount on degradation. The mass of ZVI was raised to 2.5 g and decreased to 0.5 g to provide volume-to-mass ratios of 2:1 and 8:1 for examination. These additional ratios would provide information on how17β-estradiol degradation was affected by twice and half as much ZVI mass relative to the 4:1 ratio that was initially utilized due to its establishment in the literature [18,23,24]. This variation of mass would allow for the determination of the effect that ZVI amount in relation to contaminated solution would have on degradation and allow for satisfaction of the third overall objective.

All three experimental ratios were examined at different times up to period of one week based on times seen in previously mentioned ZVI experimentations [19,24]. The samples were prepared in triplicates with deionized water to provide the most accurate experimental results. The vials were placed on an orbital mixing rotator at 40 revolutions per minute and each set was analyzed at different time intervals up to one week. For each trial, after the vials finished rotating for the appropriate time intervals, the liquid solution in the batch reactors were removed for analysis of degradation of 17β-estradiol in contact with ZVI. This methodological aspect would serve to satisfy the second overall objective in providing kinetic information on the 17β-estradiol when contacted with the ZVI. The liquid solutions were placed in 2 mL amber glass vials and stored in refrigeration until subsequent analysis using a High Performance Liquid Chromatography (HPLC).

Analyses of samples was conducted on a Shimadzu-10A HPLC system fitted with a Supelco PAH-C18 Column, and a UV-VIS Detector set at a wavelength of 230 nm [19,24]. The HPLC was comprised of an ESA model 542 auto sampler, an ESA series III pump and an ESA model 528 UV-VIS detector which provided a low detection limit of 0.01 ppm for 17β-estradiol. The carrier solution was 25% methanol, 25% acetonitrile, and 50% HPLC water purchased from Sigma Aldrich The mobile phase

flow rate was set at 2 mL/min. The analysis had a runtime of 5 minutes, with a maximum peak detected for 17β-estradiol at 1.8 minutes.

Chemicals and materials

The mobile phase solution used for quantification of 17β-estradiol consisted of 25% acetonitrile, 25% methanol, and 50% HPLC water. Acetonitrile (CH3CN) used for the mobile phase was purchased from Sigma Aldrich, with a purity of 99.9% (CAS No. 75-05-8). Methanol (MeOH) was purchased from J.T. Baker Chemicals with a purity of 99.9% (CAS No. 67-56-1). Finally HPLC grade water was purchased from Sigma Aldrich with a purity of 99.9% (CAS No. 7732-18-5). All three components of the mobile phase were completely mixed together prior to use in the HPLC machinery. Methanol extraction on the ZVI substrate was conducted to determine if any of the 17β-estradiol in solution remained trapped in the pore space and pore water undegraded to aid in evaluating the mass balance in the reactors. In these experiments liquid supernatant was removed from the batch reactor vials and MeOH was added to the top of the vials with the remaining iron leaving no headspace. The vials were re-weighed then placed on the rotator for mixing. After equilibrium was reached (>2 hours), the methanol extract was removed and placed in separate vials for analysis. The methanol was placed in contact with the ZVI in the individual batch reactors to prevent any further degradation occurring beyond the time of the sample to maintain kinetic consistency. Also, methanol was also used to remove any additional 17β-estradiol from ZVI to ensure that all of the 17β-estradiol was accounted for in degradation sample analysis and accounted for in the mass balance. All vials remained under refrigerated conditions until their analysis within the day.

Results and Discussion

The experimental results showed that when contacted with ZVI, 17β-estradiol displayed a pseudo 1st-order degradation rate function (Figures 2 through 4). The pseudo 1st-order model, when rearranged to determine degradation reaction for 17β-estradiol, can be written as [21]:

$$\frac{C}{C_0} = e^{-kt}$$

Where C represents the 17β-estradiol concentration in the solution after the degradation process has occurred; C_0 is the initial concentration of 17β-estradiol in the solution; k represents the pseudo 1st-order rate constant (hr^{-1}) for degradation of 17β-estradiol; and t is equivalent to the time that the solution was in contact with ZVI. When the plotted on a natural log-natural log scale, the generated linear slope for the experimental data gives a pseudo 1st-order degradation rate constant, -kEstradiol (hr^{-1}), also shown in Figures 2 through 4. These data were

Figure 2: Pseudo 1st-order degradation of 17β-Estradiol contacted with ZVI at a 2:1 Volume to Mass Ratio
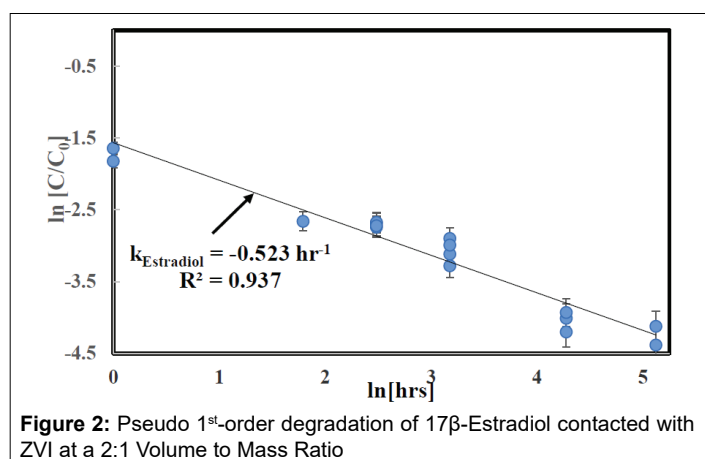
presented and calculated on triplicate samples with 95% confidence levels. In gathering these results, the first objective was completed in that 17β-estradiol in water was proven, for the first time, to degrade in the presence of ZVI, and provided the foundation for the last two subsequent objectives to be explored.

The experimentation results also allowed for examination of the degradation kinetics of the 17β-estradiol in contact with ZVI. In addressing the second overall objective for this research, the psuedo-first order degradation rate constants for 17β-estradiol were calculated for the varying ratios of volume of contaminant solution to mass of ZVI substrate within the sealed batch reactors. The degradation rate constants were 0.523 hr^{-1}, 0.425 hr^{-1}, and 0.406 hr^{-1} for the ratios of 2:1, 4:1, and 8:1, respectively. Further, based on these rate constants, the half-lives for the varying ratios were also calculated to be 1.33 hr, 1.63 hr, and 1.71 hr for the ratios of 2:1, 4:1, and 8:1, respectively (Table 2). In examining the degradation of 17β-estradiol, it was important to compare these results with other contaminants degraded by ZVI contact in aqueous systems from previous research to establish validity. Table 3 displayed the comparison of the volume-to-mass ratio of 4:1 of this present research in degradation of 17β-estradiol to other contaminants in the literature contacted with ZVI utilizing similar methodologies and volume to mass ratios [18,22, 26]. These other contaminants vary in chemical structure and include other EDCs such as bisphenol A, pesticides such as toxaphene, chlorinated organics such as trichloroethylene (TCE) and PCE, and a substituted aromatic, nitrobenzene. Though different in structure, 17β-estradiol was also shown to be effectively degraded by ZVI in aqueous systems, and compared favorably to other contaminants degradation by ZVI presented in the literature.

In addressing the third and last major overall objective, this research also explored how the amount of ZVI substrate affected the degradation of 17β-estradiol. The process of ZVI in degradation of environmental contaminants has been established to be controlled by surface reactions [21]. Therefore, as mass changes in a particular reactive system, so do the available reaction sites that allow contaminants to adsorb and react. In this research, the aqueous contaminant volume contacted with mass of ZVI present, otherwise known as the volume-to- mass ratio, was modified to examine this relationship. After gathering data based on the initial 4:1 volume-to-mass ratio used by others [24], the degradation of 17β-estradiol was examined at ratios of 2:1 and 8:1 to determine the effects of changing

Table 2: Half-lives of 17β-Estradiol degradation by ZVI at Varying Volume-to-Mass Ratios

| Volume: Mass ratio	t ½ [17β-Estradiol solution, 2ppm] (hr)
2:1	1.33
4:1	1.63
8:1	1.71

Table 3: Reaction rates and half-lives of varying contaminants in DI water treated with ZVI with 4:1 Mass to volume ratio

Contaminant	Reaction Rate	Half-lives
17β-Estradiol[a]	0.4253 hr^{-1}	1.63 hours
Bisphenol A[b]	0.0072 hr^{-1}	96.3 hours
Toxaphene[c]	0.0880 hr^{-1}	46.7 days
TCE[d]	0.0170 hr^{-1}	13.6 hours
PCE[e]	0.0037 hr^{-1}	7.72 days
Nitrobenzene[f]	2.040 hr^{-1}	0.34 hours

[a]-Current Study, [b]-Clark et al. [23], [c]-Clark et al. [21], [d]-Gillham et al. [17] , [e]-Clark et al. [19], [f]-Tratnyek et al. [25]

the available substrate mass on the overall reactions (Figure 2 through 4). As the mass of ZVI was increased and the volume-to- mass ratio reduced to 2:1, the reaction rate of 17β-estradiol increased by roughly 23%. This increase was indeed expected as the mass of ZVI was increased compared to the relative volume of 17β-estradiol in aqueous solution resulting in a greater number of sorption sites available for contaminant sorption and degradation. For the 8:1 ratio, the reduction in ZVI mass relative to contaminant aqueous volume resulted in a 4.6% decrease in degradation reaction rates. The change reaction rates relative to substrate presence can be related to the adsorption of the 17β- estradiol on the solid substrate at available active sites. Once adsorbed, the contaminant was degraded by the highly oxidative environment created when the ZVI is contacted with water. As mentioned in the methodology, it was determined that all of the 17β-estradiol was degraded and did not remain as residual on the ZVI surface. Therefore, as the available sorption sites reduced with decreasing ZVI mass, the contaminant sorption was also reduced, thereby limiting the amount of 17β-estradiol degraded. This phenomenon agreed with similar results reported in the literature [22]. The trends observed in the degradation rate coefficients extended to the half-lives for the varying volume-to-mass ratios as well (Table 2). As expected, the 2:1 ratio results with higher degradation rates displayed a lower half-life, 1.33 hours, compared to the 4:1 ratio value of 1.63 hours. Similarly, the 8:1 ratio with slower degradation rates compared to the 4:1 ratio exhibited a higher half-life of 1.71 hours (Figures 3 and 4).
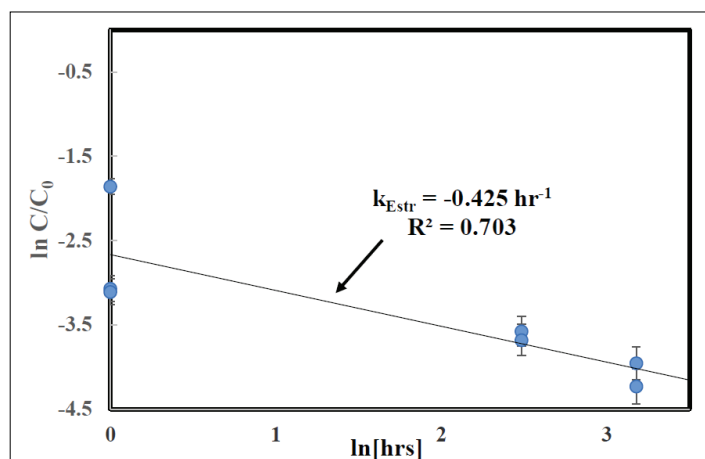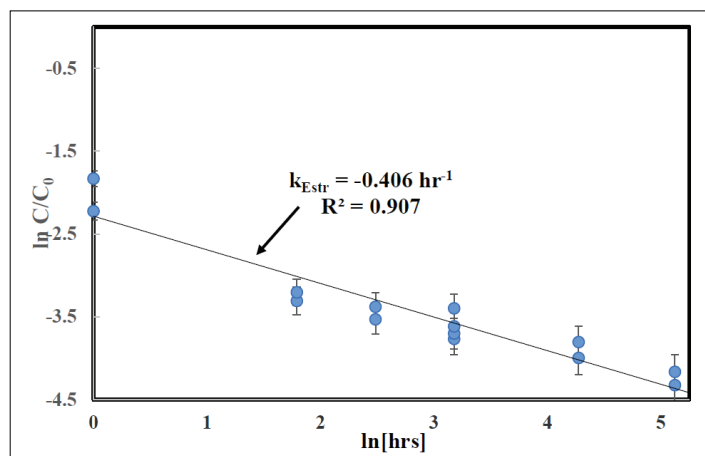
Overall, 17β-estradiol mass in aqueous solution was also shown to be effectively degraded by contact with ZVI in the present research. Based on a mass balance taken in each individual batch reactor, it was determined that over 98% of the 17β-estradiol mass degraded within the first 25 hours of the ZVI contact as shown in Figure 5. Furthermore, continued monitoring showed that this increased to nearly 99% by the end of 72 hours. These findings compare favorably to other degradation mechanisms applied to 17β-estradiol shown in the literature, especially as the present research examines a passive technology requiring no additional power added. Maniero et al. [7] showed that with varying amounts of ozone contact, nearly all of 17β-estradiol at 20 µg/L completely degraded. Bila et al. [27] also showed the effectiveness of ozone to degrade between 99.1% and 99.8% for varying pH levels. Though a more energy intensive process, more than 90% of the 17β-estradiol was degraded within 5 min by ozonation with the simultaneous addition of Mn^{2+} and oxalic acid in both the 15 and 40 µM ozonation systems [28]. These processes each have shown great effectiveness in the remediation of ozone; however, the use ZVI also has shown to match this effectiveness without requiring external power.

The major issue that has traditionally acted as a hindrance for ZVI in aqueous solutions has been the formation of iron oxides on the surface of the substrate. The oxides reduce the number of available sites that would be active to degrade the contaminants in solution [29,30]. However, after degradation of 99% of the mass of 17β-estradiol, no amount of appreciable oxide formation was noted by SEM analysis of the ZVI (Figure 6). Therefore, it could be expected that larger concentrations of

Figure 3: Pseudo 1st-order degradation of 17β-Estradiol contacted with ZVI at a 4:1 Volume to Mass Ratio
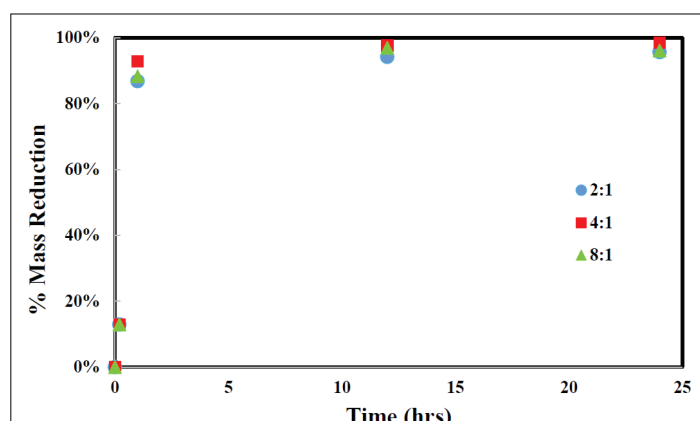
Figure 5: Percentage of Mass Reduction of 17β-Estradiol by ZVI at varying Volume to Mass Ratios

Figure 4: Pseudo 1st-order degradation of 17β-Estradiol contacted with ZVI at a 8:1 Volume to Mass Ratio
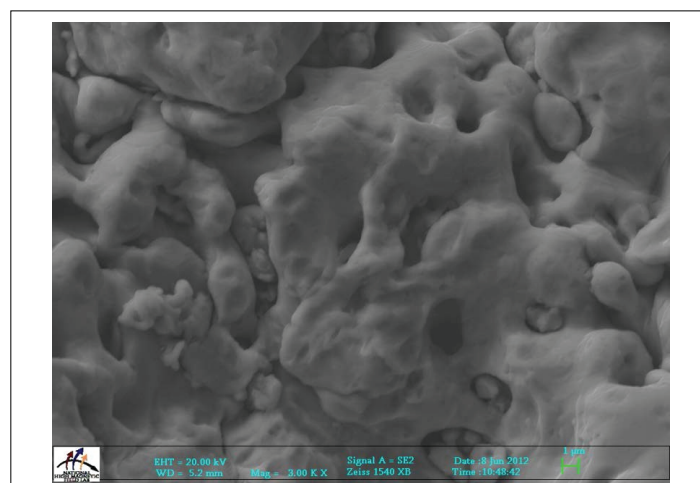
Figure 6: SEM scan of 17β-Estradiol after contact with ZVI

17β-estradiol in aqueous systems could also be degraded, though this level of contaminant is not generally found in nature especially subsequent to general wastewater treatment processes [6].

Overall, ZVI was found to effectively degrade the EDC, 17β-estradiol, in aqueous systems. This degradation of 17β-estradiol by ZVI compared favorably with other similar degraded contaminants, such as EDCs, pesticides, and chlorinated organics, in aqueous systems. As the ZVI mass increased, the greater the degradation rates and the lower the half-lives of 17β-estradiol in the systems were noted. Furthermore, the passive nature of ZVI oxidation in aqueous environments which effectively degrade EDCSs can improve the cost effectiveness, cost efficiency, and overall sustainability in remediating these contaminants from water systems.

Conclusions

The novel contribution of this research was the finding that the endocrine disrupting compound, 17β-estradiol, can be significantly degraded by ZVI in aqueous systems. It was also determined that the degradation of this contaminant was found to display a pseudo-1st order degradation reaction rate. Over the weeklong duration of the experiment, approximately 99% of the 17β-estradiol mass was degraded when contacted with ZVI in aqueous systems without discernable production of corrosion on the substrate surface.

Changing of the mass of ZVI relative to the volume of contaminant solution was also found to affect the rate of 17β-estradiol degradation. It was shown that the lower the contaminant aqueous volume and the higher the ZVI mass resulted in higher degradation rates and lower half-lives for the same initial concentration of 17β-estradiol. This relationship was attributed to the surface site availability which directly controls the degradation effectiveness on the ZVI surface as established in literature. Results of the ZVI degradation of 17β-estradiol in aqueous systems also compared favorably with other contaminants, such as EDCs, pesticides, and chlorinated organics, treated by the same methodology.

Overall, this research concluded that ZVI can be used to effectively degrade the EDC, 17β-estradiol, in aqueous systems. The optimization of this treatment process could potentially improve cost effectiveness, cost efficiency, and overall sustainability in remediating harmful and EDCs from water systems.

Acknowledgement

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