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Cost Analysis of Zero Valent Iron as a Humic Acid Pretreatment for the Forward Osmosis Hydrowell

Nikhil Shah
University of Connecticut - Storrs, nikhil.shah@uconn.edu

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Cost Analysis of Zero Valent Iron as a Humic Acid Pretreatment for the Forward Osmosis Hydrowell System

Abstract. The use of forward osmosis to treat drinking water in the developing world has been growing in interest recently. Hydration Technology Innovations has designed a forward osmosis system that effectively cleans water, creating a nutritious drink. An area of concern is the loss of productivity caused by fouling of the membrane by humic acid. In this study, the effectiveness and cost of using zero valent iron as a pretreatment for the Hydrowell system is investigated. It was found that, with the pretreatment system design used in the study, it was not cost effective to use iron as a pretreatment. The iron itself was able to remove between 37% and 64% of the humic acid from the feed water, indicating that there is a system design in which iron could be an effective filter.

1. Introduction

The lack of potable water is a problem that faces about 894 million people around the world. A vast majority of these people live in the developing world, primarily in rural areas. This poses three problems for the development of water purification technologies. First, the areas in greatest need of purification technologies are also the places with the least access to energy resources. Second, because many of the people live in remote, rural areas, there is little possibility of creating a centralized water distribution system. Third, the people often live on fewer than two dollars per day, leaving little available income for water.

Forward osmosis (FO) is a technology that has the potential to effectively address these concerns. Forward osmosis utilizes the osmotic power of a concentrated draw solution to pull contaminated water across a selectively permeable membrane, while leaving any contaminants behind. In the application of forward osmosis being investigated, the Hydrowell system manufactured by Hydration Technology Innovations (HTI), the draw solution is composed of sugars, nutrients, and other electrolytes. This solution creates a nutritious drink similar to many commercial sports drinks.

While forward osmosis requires no point-of-use energy and can be implemented at a household scale, the membrane necessary for the process is relatively expensive and requires highly skilled workers to produce. For this reason, producing the membrane locally would be impractical. It is therefore necessary to investigate a way to extend the life of the membrane and thus reduce the cost of the drink produced.

One of the primary causes of a loss in membrane life is fouling. One foulant that has been studied on the HTI forward osmosis membrane being tested is humic acid, a mixture of many organic acids (1). Zero-valent iron, used in permeable reactive barriers, has proven effective in removing organic contaminant plumes from groundwater (2).

The objective of this study is to determine the effectiveness of zero valent iron as a pretreatment option to reduce the humic acid concentration of the feed water and to analyze whether the reduction in concentration is of greater value than the cost of the iron used.

2. Materials and Methods

2.1 Materials

Zero-valent iron powder (40 mesh) was obtained from Fisher Scientific. F-75 Ottawa Silica Sand (99.77% SiO₂) was obtained from Axner Pottery Supply, Oviedo, Fl. All media was packed into columns as received, unwashed. Humic acid (technical grade) was obtained from Fisher Scientific. No purification was performed before use. A 1000x concentrated (10 g/L) humic acid stock solution was prepared and stored in a dark cabinet. All
materials to build the column were obtained from McMaster-Carr.

2.2 Experimental Setup

All column tests were run in a 1-in inner diameter by 1-ft length clear PVC column. The packed columns were gravity fed to simulate practical application in the developing world. A constant head was maintained using interchangeable “flow stabilizing columns” of 1-ft, 2-ft, and 4-ft lengths. See Figure 1 for column experiment setup.

Each column was packed as follows. A perforated stainless steel reinforcing plate was placed at the bottom of the column. A __________ was placed next to ensure no media was lost. 50 mL of filter media was funneled into each column and compacted by tapping lightly on the side of the column along the length of the media. Three filter media combinations were used: 1:1 (v:v) iron:sand, 1:3 (v:v) iron:sand, and 1:9 (v:v) iron:sand.

5 L deionized water was added to the test solution reservoir and the system run. 1 L was allowed to flush through system, washing the filter media, before humic acid was introduced. Humic acid was introduced as 1 L of 5x concentrated solution. Additional 1x concentrated humic acid solution was added as required to maintain the reservoir at an appropriate level. ~30 mL samples of the column effluent were taken at appropriate intervals and stored in a dark cabinet until analysis.

2.3 Analytical Techniques

Humic acid concentration was determined via a Fisher Scientific Genesys 10S ultraviolet–visible spectrophotometer. 3mL quartz glass cuvettes (from Fisher Scientific) with a 10mm path length were used. All samples were measure at a wavelength of 258 nm. A single sample calibration was utilized to determine absolute humic acid concentration of each sample.

3. Results

As predicted, the iron was effective in removing humic acid from the feed water causing significantly reduced concentrations in the effluent. Each iron concentration followed a similar trend, starting with high rejection and then reducing over time to a relatively stable percent rejection.

Figure 2.a. shows the percent reduction of humic acid through the 10% iron column. Because of the relatively low concentration of iron, within the first 1000 mL flow, the rejection of humic acid had fallen by more than half to remain fairly steady around 37% rejection. It is likely that the initial high rejection values were due to the humic acid solution not having reached the bottom of the column.

Figure 2.b. shows the percent reduction of humic acid through the 25% iron column. In this test, the high rejection value held for slightly longer before falling quickly to remain steady around 48% rejection.
Figure 2.c. shows the percent reduction of humic acid through the 50% iron column. The high concentration of iron in this column caused the rejection to fall more slowly and steadily out at the highest value yet of around 64%. This test breaks from the trend at the end by increasing rejection at a high filtrate volume. Based on observations of the filter media post filtration and the dramatic decrease in flow rate over the course of the test, it is predicted that the reaction between humic acid and the iron particles created a media “cake” of extremely low permeability. This cake provided surface area for settling of humic acid as well as slowed the flow rate, creating greater residence time for the humic acid solution within the filter media.

It is clear from Figure 3 that the flow rate decreases quickly with high concentrations of
iron. This could potentially make it impractical to use high iron content media as a pretreatment for the Hydrowell system.

4. Cost Analysis

4.1 Effect of Humic Acid on FO Membrane

The forward osmosis membrane that is being used in the Hydrowell system is a cellulose acetate membrane manufactured by HTI. Mi et al investigated the effect of organic fouling by humic acid on this membrane (1). In the FO experiment, a 0.002 m² membrane coupon was used. The membrane in the Hydrowell system has a surface area of 1.394 m², making it 694 times larger than the membrane coupon tested.

Figure 4, taken from Mi’s paper, shows flux reduction over time in the presence of 20 mg/L humic acid and 0.5 mM Ca²⁺. It is appropriate to use the data with Ca²⁺ added, because the Ethiopian source waters contain high levels of Ca²⁺. According to a water quality study conducted in Ethiopia, the median calcium concentration among the wells tested was 35.665 mg/L (or about 0.89 mM), well above the level tested in the FO study (3). As the FO study states that a higher concentration of Ca²⁺ would lead to a greater reduction in flux, it will be safe to use the data in Figure 4 as a “best case” scenario for analyzing cost.

Defining the variable “N” as the normalized flux reduction allows for the FO paper data to be utilized in the cost analysis.

\[
N = \frac{J_{w,j} - J_{w,f}}{\Delta V \cdot C_{HA}} \text{ (Eq. 1.1)}
\]

Where \( J_{w,j} \) is the initial water flux through the membrane, \( J_{w,f} \) is the final water flux, \( V_p \) is the permeate volume, \( A \) is the surface area of the membrane, and \( C_{HA} \) is the concentration of humic acid. This assumes that each of the relationships is linear. In the case of the HTI membrane:

\[
N = \frac{(7.6 - 4.9)}{0.900 \left( \frac{20}{0.002} \right)} = 3.9 \times 10^{-5} \text{ m}^2 \text{ mg}^{-1}
\]

This is the percent water flux reduction caused by humic acid for every liter of permeate normalized with respect to humic acid concentration and surface area of the membrane.

4.2 Cost of Running the Hydrowell System

The base cost of running the Hydrowell system is a composite of three prices: the initial cost of the membrane and the recurring costs of the draw solution and cleaning reagents. For the sake of simplicity, the system is assumed to run for 24 hours a day. Thus the total volumetric cost of the clean drink is given by:

\[
P = \frac{P_m + P_{d,s} + P_{cr}}{V_{cd}} \text{ (Eq. 2.1)}
\]

Where \( P_m \) is the cost of the membrane, \( P_{d,s} \) is the system cost of the draw solution, \( P_{cr} \) is the cost of the cleaning reagent, and \( V_{cd} \) is the total volume of clean drink produced. The cost of the membrane is $291.

The system cost of the draw solution varies on two parameters: cost per liter of draw solution and dilution factor of the drink. The
cost per liter of draw solution sold by HTI is $12.20, however, in order to maximize the sustainability of the system, it is anticipated that the draw solution will be made locally where the system is being used. It is impossible to know the cost of making the draw solution in Ethiopia without traveling there, and so the cost will remain a variable with an upper bound of $12.20.

The dilution factor is the percentage of clean drink that is draw solution.

\[ d = \frac{V_{ds}}{V_{cd}} \quad (\text{Eq. 2.2}) \]

Where \( V_{ds} \) is the volume of draw solution used and \( V_{cd} \) is the total volume of clean drink produced.

The dilution factor of the drink changes based on the flow rate of the system. Table 1 shows the HTI advertised flow rate versus dilution factor.

<table>
<thead>
<tr>
<th>Flow Rate (L/day)</th>
<th>Dilution Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>0.026</td>
</tr>
<tr>
<td>24</td>
<td>0.034</td>
</tr>
<tr>
<td>30</td>
<td>0.041</td>
</tr>
</tbody>
</table>

The system cost of draw solution can now be calculated using:

\[ P_{ds,v} = P_{ds,v}L_dQd \quad (\text{Eq. 2.3}) \]

Where \( P_{ds,v} \) is the volumetric cost of draw solution, \( L_d \) is the lifetime of the membrane in days, \( Q \) is the flow rate, and \( d \) is the dilution factor.

The Hydrowell system needs to be cleaned once a week to avoid biofouling of the membrane. The cleaning reagent currently used is sodium metabisulfite, a biocidal agent. This means that it is unlikely to be effective in removing humic acid fouling.

The total cost of cleaning the system is:

\[ P_{cr} = P_{cr,w}L_w \quad (\text{Eq. 2.4}) \]

Where \( P_{cr,w} \) is the weekly cost of cleaning reagent and \( L_w \) is the lifetime of the membrane in weeks.

The price per weekly cleaning can be found with:

\[ P_{cr,w} = P_{cr,g}C_{cr}V_{cr} \quad (\text{Eq. 2.5}) \]

Where \( P_{cr,g} \) is the cost per gram of cleaning reagent, \( C_{cr} \) is the percent mass concentration of cleaning reagent solution, and \( V_{cr} \) is the volume of cleaning reagent used. This assumes the density of water is 1 g/mL and that the addition of sodium metabisulfite provides no volume change to the solution.

The cost per gram of cleaning reagent is $0.09/g. The percent mass concentration of cleaning reagent solution is .14. The volume of cleaning reagent used is 10 mL. Therefore the price per weekly cleaning is:

\[ P_{cr,w} = 0.09 \times 0.14 \times 10 = \$0.13/\text{week} \]

Substituting this value into Eq. 2.4 gives:

\[ P_{cr} = 0.13L_w \quad (\text{Eq. 2.6}) \]

Substituting the component costs into Eq. 2.1 gives the total volumetric cost of running the system.

\[ P = \frac{291 + P_{ds,v}L_dQd + 0.13L_w}{L_dQ} \quad (\text{Eq. 2.7}) \]

Figure 5 was constructed using the advertised lifespan of the untreated (i.e. fouled) membrane of 90 days. The three flow rates used are those given in Table 1. The highlighted regions are those in which the particular flow rate is the cheapest operating rate.

4.3 Effect of Pretreatment on the Cost of Running the Hydrowell System

The addition of the pretreatment system affects only the flow rate of the system directly. The change in flow rate will in turn affect the longevity of the membrane and therefore the
Cost of Clean Drink for Untreated Membrane

![Graph showing cost per liter of drink produced vs. cost per liter of draw solution.]

16 L/day —— 24 L/day —— 30 L/day

Figure 5.

cost. Rearranging Eq. 1 provides the percent flux reduction caused by adding humic acid to the Hydrowell system.

\[
\frac{(J_{W,J} - J_{W,J})}{J_{W,J}} = NAV_p C_{HA} \quad A \quad \text{(Eq. 1.1)}
\]

Substituting the values from the Hydrowell system gives:

a. 16 L/day

\[
\frac{(J_{W,J} - J_{W,J})}{J_{W,J}} = (3.9 \times 10^{-5})(1440) \left( \frac{10}{1.394} \right) = 0.40
\]

b. 24 L/day

\[
\frac{(J_{W,J} - J_{W,J})}{J_{W,J}} = (3.9 \times 10^{-5})(2160) \left( \frac{10}{1.394} \right) = 0.60
\]

c. 30 L/day

\[
\frac{(J_{W,J} - J_{W,J})}{J_{W,J}} = (3.9 \times 10^{-5})(2700) \left( \frac{10}{1.394} \right) = 0.76
\]

Thus the setup that provides for 16 L/day production of clean drink is, over the lifetime of the membrane, losing 40% of its optimal production. The 24 L/day setup is losing 60% of its optimal production. The 30 L/day setup is losing 76% of its optimal production.

The iron pretreatment does not remove all the humic acid from the feed water. It is therefore necessary to modify the percent flux reduction based on the iron pretreatment used.

Because of the intrinsic limitations of the membrane to reach high fluxes, the flux inefficiencies will be translated into longevity increases. The results are shown in Table 2.

<table>
<thead>
<tr>
<th>Flow Rate</th>
<th>10% Iron</th>
<th>25% Iron</th>
<th>50% Iron</th>
</tr>
</thead>
<tbody>
<tr>
<td>16 L/day</td>
<td>106 days</td>
<td>111 days</td>
<td>121 days</td>
</tr>
<tr>
<td>24 L/day</td>
<td>116 days</td>
<td>126 days</td>
<td>146 days</td>
</tr>
<tr>
<td>30 L/day</td>
<td>125 days</td>
<td>142 days</td>
<td>175 days</td>
</tr>
</tbody>
</table>

In addition to calculating the increased longevity of the membrane, it is necessary to factor in the cost of the iron. The cost of the sand will be considered negligible in determining the cost of the system. Adding an extra term to Eq. 2.1 gives:

\[
P = \frac{P_m + P_{dx} + P_{cr} + P_i}{V_{cd}} \quad \text{(Eq. 3.1)}
\]

Where \(P_i\) is the cost of the iron pretreatment.

To calculate the cost of the iron over the lifetime of the membrane, it is necessary to determine at what point the iron is no longer acting as an effective pretreatment. With the design used in these tests, the head loss caused by the humic acid reacting with the iron is the limiting factor. Thus, "exhaustion" will be considered the time at which the flow rate of the iron column drops below the flow rate of the Hydrowell system. Table 3 shows the volume filtered at the crossover point.

<table>
<thead>
<tr>
<th>Flow Rate</th>
<th>10% Iron</th>
<th>25% Iron</th>
<th>50% Iron</th>
</tr>
</thead>
<tbody>
<tr>
<td>16 L/day</td>
<td>5.42 L</td>
<td>6.02 L</td>
<td>5.56 L</td>
</tr>
<tr>
<td>24 L/day</td>
<td>4.15 L</td>
<td>4.14 L</td>
<td>4.67 L</td>
</tr>
<tr>
<td>30 L/day</td>
<td>2.87 L</td>
<td>2.22 L</td>
<td>3.76 L</td>
</tr>
</tbody>
</table>
The cost of iron pretreatment can now be calculated using:

\[ P_i = \frac{V_{cd} - dV_{cd}}{V_b} P_{p,i,b} \]  
(Eq. 3.2)

Where \( V_b \) is the volume of water that can be filtered with each batch and \( P_{p,i,b} \) is the price per batch of iron used. The \( -dV_{cd} \) is included to remove the draw solution volume from the total volume of clean drink produced.

Substituting the expanded price of iron pretreatment, as well as the other component prices, into Eq. 3.1 gives the total pretreated price of water.

\[
P = \frac{291 + P_{d,i,b} L_d Q_d + 0.13L_o + \frac{V_{cd} - dV_{cd}}{V_b} P_{p,i,b}}{L_d Q}
\]  
(Eq. 3.3)

Substituting the constant values into Eq. 3.3 provides the graph in Figure 6. The labels on the graph follow the pattern flow rate/percent iron.

Cost of Clean Drink for Treated Membrane

![Graph showing cost per liter of clean drink produced vs cost per liter of draw solution](image)

Figure 6

5. Conclusion

From Figure 6, it is clear that for every combination of flow rate and percent iron pretreatment, the cost of water is greater than for the untreated system. This leads to the conclusion that it would not be cost efficient to use an iron pretreatment system to remove humic acid from the water.

The primary cause of the great increase in price is the fact that the limiting factor for iron “exhaustion” is that the flow rate falls below the flow rate of the Hydrowell system. That condition, however, is not very efficient because it requires that some amount of unexhausted iron is disposed of every batch. This can easily be fixed by reducing the height of the media in the column so that exhaustion occurs before the flow rate drops too far. This could significantly decrease the cost of the iron while retaining the extended longevity of the membrane.

6. Future Work

There are four primary areas of research that need to be conducted before this cost analysis can be considered accurate. First, it will be necessary to study the accessibility of humic acid into the Hydrowell membrane. The study by Mi et al. used a cross flow system as a way to analyze overall membrane fouling. This allowed the entire membrane to be available for fouling during the entire test. The Hydrowell system uses a spiral wound membrane and so there is neither a continuous cross flow nor equal access to the membrane during filtration. Both of these lead to Eq. 1’ providing much higher values for percent flux reduction than would be realistically achieved.

The second area of study would be to determine the effect of the other forms of fouling. Biofouling and scaling can both cause decreased flux through the system and a shorter life for the membrane.

The third area of study would be to redesign the system so that exhaustion of the iron occurs before the flow rate drops below that of the Hydrowell system.
Finally, a long term analysis of the Hydrowell system will be necessary to determine if the advertised flow values are accurate.

7. Acknowledgements

I would like to thank Dr. Jeffrey McCutcheon for the use of his lab and his support throughout this entire project. I would also like to thank Jason, Dan, and the other members of SWELL who helped me troubleshoot at every step of design and testing. I would like to thank Ethan Butler and the rest of the Ethiopia Lab Group for their work in advancing the Ethiopia Project. A special acknowledgement to Hydration Technology Innovations for the donation of several Hydrowell systems for the Ethiopia Project.

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8. References

