

Sustainable Iron Removal from Groundwater Supporting Aquaculture

Basic Information

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Principal Investigators:	Ron Malone, Donald Dean Adrian

Publications

There are no publications.

Synopsis

Problem and Research Objectives

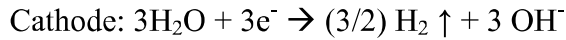
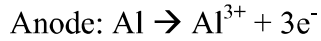
This project built scientific foundation to facilitate the development of simplified approaches to the removal of iron in a rural environment. The targeted beneficiary of this effort is the aquacultural industry in the state. Aquacultural facilities in the state generate over 100 million dollars of product including industries such as catfish, tilapia, turtles, alligators, soft crabs, and crayfish. Many of these facilities are located in rural areas and their processes require a relatively high volume of freshwater from wells. As well water is considered disease free; it is the preferred water source. However, iron is toxic to most fish and crustaceans at low levels and is seen as problematic in a number of locales. Iron contamination of wells, for example, has been cited as a factor inhibiting soft crayfish production as early as 1990 (Culley & Doubinis-Grey, 1990). It is estimated that 8 percent of the Louisiana groundwater withdrawals are used for aquacultural purposes (Todd et al., 2008). With usage estimated at nearly 150,000 acre-feet/year, Louisiana is ranked fifth in the country for aquaculture groundwater withdrawals (Hutson et al., 2004). However, iron contamination is a problem in many parts of the state, as aquatic animals, fish and crustaceans, are sensitive to free iron concentrations in water, with concentrations above 0.15 ppm generally considered toxic (Timmons & Ebeling, 2010). Iron is a common contaminate in Louisiana groundwaters where it is rapidly released from iron rich soils wherever oxygen depletion leads to ferric iron reduction. LADEQ (2006) reports several of our major aquifers display mean iron concentrations above 1 ppm . The two main alluvial aquifers display mean values over 5 ppm (Red River) and 8 ppm (Mississippi River). Iron is also a common problem in shallow rural wells which are impacted by organically rich surface soils. Although iron removal techniques are well identified (Tchobanoglous et al., 2003), the aquacultural industry generally lacks a cost effective means of treating the high volumes of water their industry demands. Similar iron problems exist in adjacent states (Todd et al., 2008).

Floating bead filters that integrate biofiltration and physical filtration into a single unit are known as “bioclarifiers”. These units have been used successfully to simplify water treatment in recirculating aquaculture systems. In recent years, traditional treatment sequences have been reduced from several components to as little as two (a bioclarifier and an airlift), which operate with dramatically less impact on the environment. Energy consumption has been reduced by over fifty percent compared to recirculating designs of the late 1990’s. These units are washed pneumatically, refiltering their own backwash waters, reducing the discharged waste water to less than 1 percent of a similarly sized sand filter (Malone and Gudipati, 2006).

Adoption of the floating bead technology will be dependent on the impact of the oxidation step on the particle size distribution of the iron hydroxides produced. Floating bead filters using standard 2-3 mm spherical bead can achieve 100 percent removal of particles above 50 microns (Drennan et al., 1994). Removal efficiencies decline to about 30 percent per pass when the particle size drops to the 5-10 micron range. The bead filters removal break point (50 microns) is almost midway between a sand filter (about 20 microns) and a settling tank (100 microns) (Ahmed 1996).

Application of an electro-coagulation technique was anticipated to accelerate the rate of formation, and ultimately, the size of floc produced in an iron removal process. Electrocoagulation of iron has been proved as an effective method of iron removal (Ghosh et al., 2008). The hydroxide flocs formed in the process act as adsorption sites for iron. EC process has gained importance because of its high removal efficiency, no use of chemicals, no secondary harmful disposal pollutant generation, and less time requirement. In the process of electrocoagulation, sacrificial metal anode dissolves thus, generating the coagulant species.

Immediate generation of hydrogen can be seen at cathode. This sacrificial anode is responsible in the precipitate formation and adsorption of contaminants from water. Reactions at respective electrodes are shown here (Aluminum electrode has been used) (Ghosh et al., 2008):



The amount of Aluminum (Al^{3+}) released at different currents is calculated according to Faraday's second law of electrolysis:

$$x \text{ (gm)} = \frac{A \times T \times MW}{96484.56 \times e^{-}}$$

Where;

x : mass of substance released or consumed in grams

A : Amount of current passed in Amperes

T : Time for which the current was passed in seconds

MW : Molecular weight of the substance released or consumed

e^{-} : number of valance electrons in 1 mole of substance

This project evaluated the application of an electro-coagulation and floating bead filter combination to the iron removal for aquaculture. Specific objectives addressed included:

- 1) Determine the likely cause, and a means of avoidance, of mineral coatings that caused the loss of buoyancy in early floating bead filter iron removal applications.
- 2) Define operational guidelines for key parameters (aluminum dosage, flow, recirculating flow, pH, and retention time) required to reduce total iron levels to a level (1 ppm) safe for aquacultural applications.

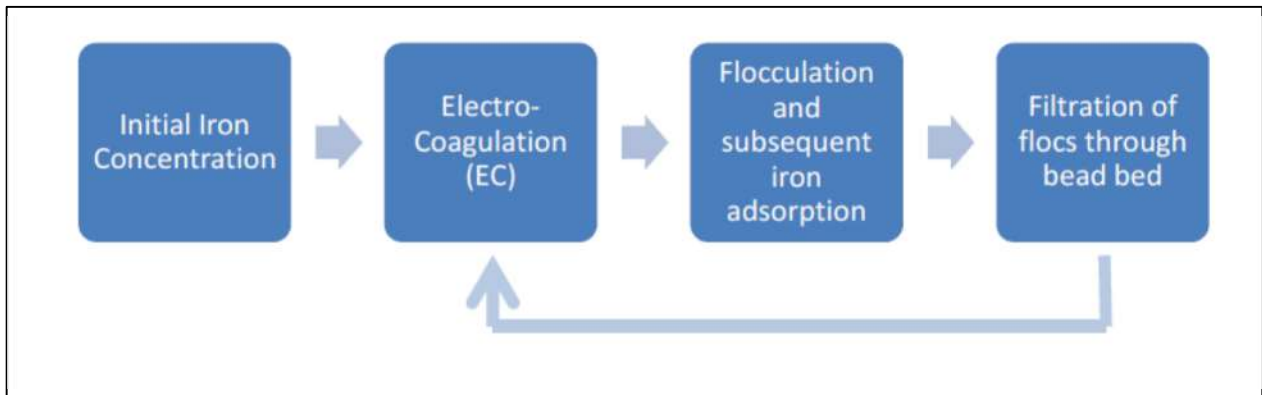
Methodology

Iron removal from groundwater has caused problems while using floating bead filters. Failure of one such filter installed on New Roads on Mississippi River due to heavy iron coating around the polyethylene beads lead to further investigation of the issue. Literature review suggested that the coat formation around media is caused by adsorption mechanism which is the adsorption of contaminant particles to the media surface (Benjamin, 2013; Sharma, 2001). Dissolved oxygen content and pH are the key factors governing the coat formation. Ferrous iron gets adsorbed onto the beads which are then oxidized to ferric in the presence of oxygen.

To check on the iron coat formation on the beads a small batch experiment was conducted. The experiment was carried out in a 1.5 Liter volume capped plastic container. The container was first filled with 1 liter deionized water. The dissolved oxygen and pH of the water was then recorded. Sodium sulfite was then added to this water to scavenge out the dissolved oxygen. After dropping the dissolved oxygen content, the pH was monitored. The pH of water shoots up to about 8 after adding sodium sulfite to it. The pH was then lowered and set to 6.5 by bubbling in CO₂ gas. Thus, the initial conditions for starting the experiment are a pH of 6.5±0.1 and dissolved oxygen amount between 0 to 0.1. Iron in the form of ferrous sulfate and ferrous chloride were tested individually. Five grams of these which is equivalent to 1.84 gm-Fe/L and 2.2 gm-Fe/L of these were added to the container and mixed thoroughly. Dry polyethylene floating beads weighing 200 grams were then added to the container. Total bead surface area available for adsorption was 10054 cm². The beads were kept moving on a magnetic stirrer (Corning PC-220 Hot Plate/Stirrer) set at the lowest speed permitted by the machine which is 60 rpm. Experiment was run for three days. At the end of three days, air was bubbled in the container for 10 minutes to increase the oxygen content of water. Beads were then separated out

and kept for drying. The dried beads were then weighed with increases in weight attributed to ferric hydroxide accumulations.

The apparatus used for running the iron removal experiments consisted of a 4 foot long, 6 inch diameter (ID) acrylic coagulation tank and a 3 foot long, 4.5 inch (ID) acrylic pipe with a 9 inch bead bed. The two cylinders were connected by ¾ inch PVC piping. Water from the electrocoagulation tank was fed by gravity through the bead bed, then was lifted back to the electro-coagulation tank by a centrifugal pump. The effective system volume was 26.1 liters. The pH of water was generally maintained between 8.0±0.3 by adding sodium bicarbonate. Temperature was set to 25°C. Iron was added in the form of 5 mg-Fe³⁺/L of ferric as ferric chloride. Flat aluminum electrodes having dimension 1-1/2” X 1/16” X 46” were used in the electro-coagulation. These plates were connected to a Mastech DC power supply. The experiments were run in a recirculating batch mode with an initial iron concentration of 5 mg-



Fe³⁺/L. Flow chart for the batch mode with recirculating flow is given in Figure 1.

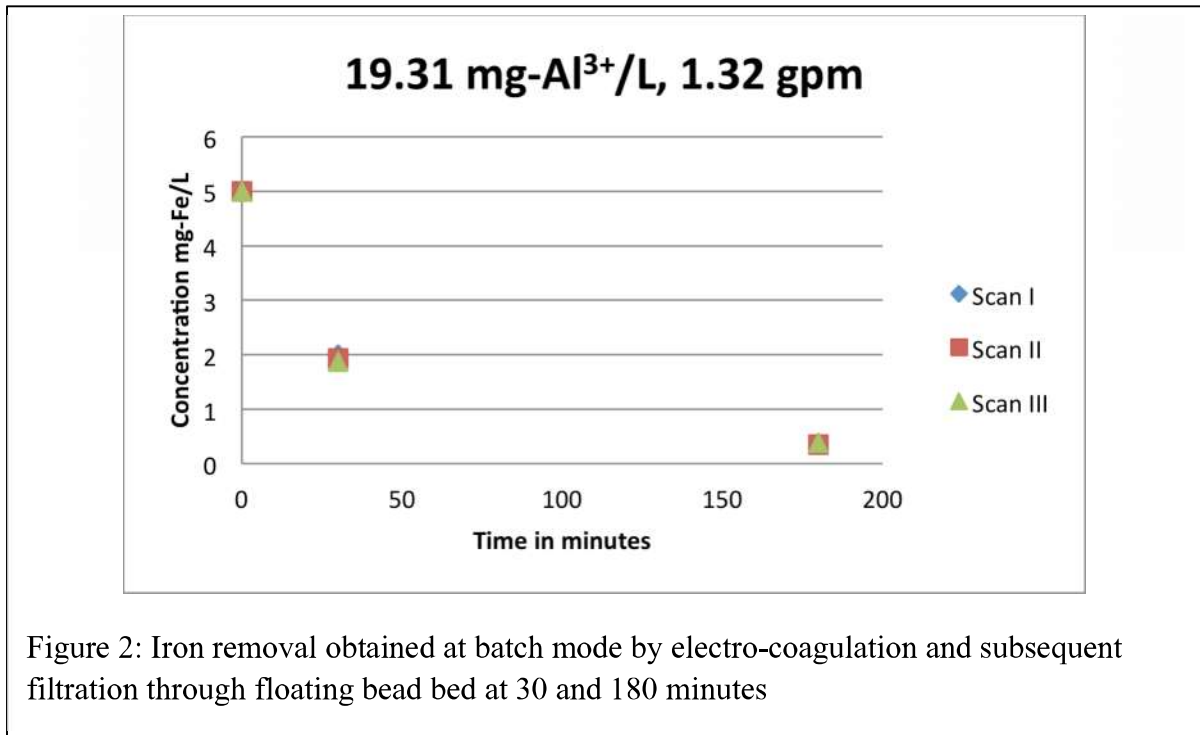
Figure 1: Flow chart representing experimental steps under batch mode of influent with an internally recirculating flow

Results and Discussion

The results of the iron coating studied confirmed that conditions commonly associated with shallow Louisiana groundwaters, i.e. a pH <7.0 and low dissolved oxygen, are conducive to

coating of plastic beads. Visible iron coatings were observed when the beads were exposed to iron rich waters while the pH was near 6.5. Mineral accumulation rates ranged from $0.033\text{mg}/\text{cm}^2$ and $0.0431\text{mg}/\text{cm}^2$ after three days dosed with ferrous sulfate and ferrous chloride, respectively. Accumulations were not observed, however, whenever the pH was maintained above or whenever the water was well aerated. These findings are consistent with a two-step coating process. First ferrous iron precipitates on the surface as ferrous hydroxide, then as oxygen becomes available the surface hardens as the ferrous hydroxides are converted to ferric hydroxides. Polyethylene beads do not have any negative surface charge and do not attract the positive ferrous ions as compared to sand which readily adsorbs iron to its surface because of its negative surface charge. While arguably pre-coating plastic beads could improve iron removal rates, it is clear that the sinking of beads by iron coating can be avoided by well aerating waters prior to filtration. This approach strips the elevated carbon dioxide commonly associated with shallow groundwaters raising the pH while promoting the rapid formation of ferric iron hydroxides.

Success of the iron removal strategy evaluated here is predicated on the electrocoagulation in a unit's ability to form floc particles in a size range (>30 microns) that is readily removed by a bed of 2-3 mm beads (Ahmed, 1996). To further compensate for weak lower end removal capabilities the water is recirculated through the process providing for multiple filtration passes. As Figure 2 illustrates, the use of electro-coagulation with a recirculating floating bead filter is capable of reproducibly removing iron down to about $0.3\text{ mg}/\text{L}$. However, the process requires a treatment process of about 180 minutes. Figure 2 represents the results obtained on passing 3 amperes of current for 30 minutes. The flow rate was set to 1.32 gpm ($12\text{ gpm}/\text{ft}^2$ of filtration flux rate).



This process proved to be relatively insensitive to dosage as seen in Figure 3 with the best removal being observed at lower Al³⁺ dosage rates tested (6.43 mg-Al³⁺/L). These results are consistent with the Metcalf and Eddy Inc., 1991 definition of 1.8 to 5.4 mg-Al³⁺/L as the optimum range for floc formation in water treatment plants using alum. Since the floc was constantly being removed as the electro-coagulating plates provided the dose over a 30 minute period, the peak aluminum dosage undoubtedly fell within the optimum range. Increasing the aluminum dosage by raising the amperage dramatically improved aluminum hydroxide floc production, but, had little impact on iron removal rates.

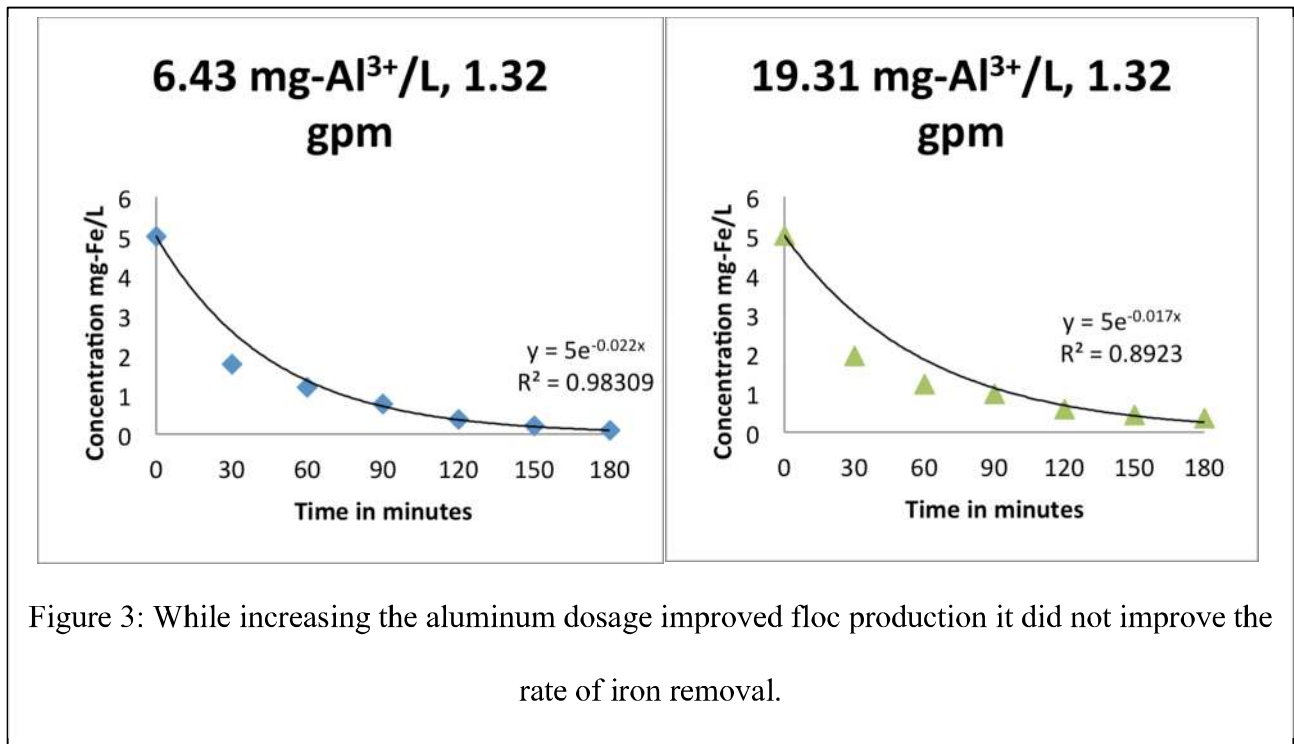


Table 2 presents the results of several comparable iron removal runs conducted at background pH of about 8.2 dosed initially with 5 mg-Fe⁺⁺⁺/L. Iron removal below the 1 ppm target was not achieved within 30 minutes under any conditions. As illustrated here, it was achievable with a retention time of 180 minutes. After 30 minutes the water in the system was passed through a through 0.2µm pore size filtration process revealing that the residual iron is particulate in form. Yet, variation in the recirculating flow, which presumably would improve the floating bead bed's ability to small particles by increasing the number of filtration passes, was found to have little impact on the process efficiency. These observations indicate that the aluminum electro-coagulation process is limited in its ability to scavenge small iron precipitates, or, that the process is time limited.

Table 2: Average of iron removals obtained at different system conditions with initial iron concentration as 5 mg-Fe³⁺/L, temperature 25°C and 30 minutes of current flow.

Current (Amps)	Equivalent Al ³⁺	pH	Recir. Flow	Internal turnover	Residual Iron* (mg-Fe ³⁺ /L)
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	dosage mg-Al ³⁺ /L		(gpm)	time (min)	30 min	180 min	Filtered **
1	6.43	8.25	0.11	43	1.83	--	0.11
1	6.43	8.27	0.33	14.3	2.11	--	0.06
1	6.43	8.31	1.32	3.59	1.66	0.10	0.11
3	19.31	8.28	0.11	43	1.77	--	0.12
3	19.31	8.16	0.33	14.3	2.10	--	0.29
3	19.31	8.22	1.32	3.59	1.61	0.36	0.31
6	38.62	8.20	0.11	43	1.81	--	0.07
6	38.62	8.22	0.33	14.3	2.25	--	0.21
6	38.62	8.26	1.32	3.59	2.04	--	0.19
* means of triplicates ** Filtered iron concentration (through 0.2µm pore size) at the end of 30 minutes							

In summary, the results of this work provide guidance for the avoidance of the formation of iron precipitates on the surface of floating beads. The results suggest that thoroughly aerating well water before contact with the bead bed will avoid the problem of coating, then sinking floating plastic beads. The combination of electro-coagulation with aluminum plates in recirculation with a floating bead bed was shown to be capable of removing residual iron concentrations to a level well below a 1 ppm iron level considered suitable for aquaculture applications. However, without pH adjustment, the process treatment time was long with approximately 75 minutes being required to reach 1 ppm for the best combination of operational parameters. A wide range of operational conditions were capable of achieving the 1 ppm objective in about 120 minutes. This extended treatment time would limit practical application

to low flow demand requirements associated with recirculating aquaculture systems. The size of reactor tanks limiting its value for high demand applications (ponds or flow through tank systems). The extended treatment time is attributed to the formation of extremely small iron precipitates that showed little affinity for aluminum flocs formed by the electro-coagulation process. These fine precipitates were only slowly removed by 1-2 mm bead beds employed.

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