

# POTENTIAL ANIONIC SORBENT USE OF IRON OXIDES FROM ABANDONED MINE DRAINAGE DISCHARGES<sup>1</sup>

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**Abstract.** This study examines the potential to reuse mine-drainage derived iron oxides as anionic sorbents for sustainable water treatment purposes. Pure iron oxides have been established as effective sorptive media or coatings for water treatment processes; yet, iron oxides from mine drainages remain to be an abundant but unproven source of this raw material. Iron oxides from both passive mine drainage treatment systems as well as environmental discharges of mine water and their associated iron deposits were examined. Based on prior physical characterization, three samples were selected (according to their specific surface area) to evaluate their anionic sorptive capacities pertaining to naturally occurring concentrations of orthophosphate ( $1.13 \pm 0.03$  mg/L) in surface waters, and arsenate ( $117.79 \pm 4.08$   $\mu$ g As/L) in drinking waters. The mine drainage derived iron oxides' performances were compared against a commercial grade iron oxide product, Bayoxide E33 P at static pH values of 6.00, 7.00, 8.00, and  $9.00 \pm 0.10$  standard pH units via laboratory scale sorption batch experiments. As a result of these experiments it was observed that the mine drainage derived iron oxides were more effective at contaminant removal than the commercial product. Promising contaminant removal efficiencies of up to 95% (arsenate) and 99% (orthophosphate) were documented at specific pH values for the mine drainage derived iron oxides, while adhering to virtually all US EPA primary and secondary drinking water standards; thus suggesting that it may be feasible to beneficially reuse mine drainage derived iron oxide in water treatment technologies.

**Additional Key Words:** Passive Treatment, Sorption Experiments

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## **Introduction**

The potential use of iron oxides in sorptive filtration technology is an intriguing proposal that currently is being studied (e.g., Dixit and Hering, 2003; Heal et al., 2005; Zeng et al., 2008; Boujelben et al., 2008; Sibrell et al., 2009; Penn et al., 2007). Sorptive filtration is the combination of conventional packed bed filtration techniques coupled with the principles of direct adsorption (Katsoyiannis and Zouboulis, 2002). The use of this filter combination increases the performance of the filter by enabling it to remove particulates from the water by filtration processes and ions from the water via surface adsorption. Iron oxide is a prime candidate to be used as a coating in mixed media filtration applications (or in pelletized form) because it has a large specific surface area and possess a high affinity to form surface complexes with cations and anions that are in solution (Zeng et al., 2008; Dzombak and Morel, 1990; Benjamin and Leckie, 1981). The ability of iron oxides to remove both cations and anions from solution is largely dependent upon the pH point of zero charge ( $\text{pH}_{\text{pzc}}$ ) inherent to each iron oxide sample. Various mining related impurities that have become incorporated into the iron oxide particle structures are site specific in nature, thus allowing for a wide range of  $\text{pH}_{\text{pzc}}$  values to exist (Kairies et al, 2005). For instance, if the pH of solution is below the  $\text{pH}_{\text{pzc}}$  of an iron oxide, the resulting surface charge is positive; therefore promoting the enhanced removal of anions from solution. While in the opposite scenario, where the pH of solution is above the  $\text{pH}_{\text{pzc}}$  of the iron oxide, the surface charge is negative and cation removal will be favored (e.g., Ahmed & Maksimov, 1968; Pechenyuk, 1999; Dzombak and Morel, 1990; Kairies et al., 2005).

This study examines the water treatment capabilities of recovered mine drainage derived iron oxides from the Mayer Ranch Passive Treatment System (MR), Panola Seep #2 (PS2), and Gowen Battles Seep (BS), while evaluating their removal efficiencies with respect to the commercial grade synthetic iron oxide, Bayoxide E33 P (BAY). The physical/chemical characteristics of Bayoxide E33 P displayed in Table 1 were obtained from the material safety data sheet provided by the manufacturer, LANXESS. A previous study performed by Neely and Nairn (2010) provides a detailed account of the methods used for sample collection, preparation, and characterization of 13 mine drainage derived iron oxides, including the three iron oxides used in this study. Water quality and dissolved metals data for the 13 mine water sources (12 coal and one hard rock) were analyzed to aid in correlating site specific mine water conditions and dominant forms of iron oxide present at each location. The iron oxides used in the current

study were selected based on their respective BET specific surface areas (MR 267.6 m<sup>2</sup>g<sup>-1</sup>, PS2 124.8 m<sup>2</sup>g<sup>-1</sup>, BS 58.5 m<sup>2</sup>g<sup>-1</sup>, BAY 120-200 m<sup>2</sup>g<sup>-1</sup>) to ensure iron oxides that possessed specific surfaces areas smaller, similar to, and larger than the commercial product were examined.

Table 1. Characteristics of Bayoxide E33 P

Physical Characterization	
Color	Yellow (pigment 42)
% Synthetic $\alpha$ -FeOOH	> 70
Particle Density (g/cm <sup>3</sup> )	3.6
Specific Surface Area (m <sup>2</sup> /g)	120 - 200
Water Content (Maximum %)	20
Sieve Analysis (% < 0.5 mm)	10
Sieve Analysis (% > 2.0 mm)	5
Trace Metal Analysis (Maximum mg/kg)	
Al	350
Ba	10
Co	100
Cr	250
Cu	100
Mn	3,000
Ni	300
Pb	3
Zn	100

Waters contaminated with naturally occurring levels of orthophosphate (PO<sub>4</sub><sup>3-</sup>) and arsenate (AsO<sub>4</sub><sup>3-</sup>, oxidation state +5, As(V)) at pH values between 6 and 9 were examined through laboratory scale sorption experiments to determine if it would be practical to utilize mine drainage derived iron oxides to treat contaminated source waters. Specifically, the removal of low concentrations of PO<sub>4</sub><sup>3-</sup> in an effort to prevent eutrophication (initial concentration ~1,000 µg PO<sub>4</sub><sup>3-</sup>/L; mesotrophic treatment goal 10 - 30 µg total P/L) has been examined in detail due to the fact that previous studies have primarily focused on high concentration PO<sub>4</sub><sup>3-</sup> removal capabilities. The narrow focus of previous studies that have only examined high concentration PO<sub>4</sub><sup>3-</sup> removal has created a void in the research pertaining to the removal of PO<sub>4</sub><sup>3-</sup> from surface

waters at lower, naturally occurring levels. Additionally, drinking water contaminated with  $\text{AsO}_4^{3-}$  (initial concentration  $\sim 100 \mu\text{g As/L}$ ) was evaluated to determine the feasibility of using mine drainage derived iron oxides as a sorptive media to attain the United States Environmental Protection Agency (US EPA) primary drinking water standard of  $10 \mu\text{g As/L}$ .

### Phosphorus

Eutrophication of surface water is a condition that involves excess nutrients (primarily nitrogen and phosphorus), which are often inadvertently introduced into a body of water through the land application of fertilizers or municipal wastewater discharges, thus initiating the deterioration of water quality. According to Pace and Groffman (1998) total phosphorous concentrations such as those shown in Table 2 are commonly associated with four distinct freshwater trophic states.

Table 2. Total phosphorus concentration thresholds ( $\mu\text{g/L}$ ) for freshwater trophic states

Trophic State	Total Phosphorus
Oligotrophic	< 10
Mesotrophic	10 to 30
Eutrophic	30 to 100
Hypertrophic	> 100

Elevated levels of nutrients fuel large algal blooms that occur during specific times of the year when growth conditions are optimal. Die off of these algal blooms is directly responsible for the severe depletion of dissolved oxygen levels. This condition is a form of water pollution that places a stranglehold on life within the body of water and it is becoming increasingly prevalent in many industrialized and developing countries throughout the world (Correll, 1998). Runoff from agricultural operations (non-point source pollution), as well as effluent concentrations from wastewater treatment plants (point source pollution) are two of the prominent sources of nutrient inputs to surface waters.

Of late, various wastewater treatment facilities are utilizing constructed wetlands as a form of tertiary treatment for nitrogen and phosphorus sequestration (Vesilind, 2003). With the current

application of such wetlands, nitrogen is effectively retained within the wetland helping to minimize the potential effects of eutrophication. However, these constructed wetlands are not currently configured in a manner that accounts for the efficient retention of phosphorus, the other major contributor of eutrophication. This shortcoming reinforces the need for a method of enhanced P removal to be developed. Kang et al. (2003) have investigated the use of iron oxide particles as sorbents to enhance phosphorus removal from secondary clarifiers at the Gyeongsan City wastewater treatment plant, South Korea. Conventional tertiary treatment methods for P removal include the addition of Fe and Al salts to precipitate  $\text{PO}_4^{3-}$  in solid form, as either Al or Fe phosphate (Crittenden et al., 2005). Replacing the use of cost intensive materials with readily available iron oxides remains an alternative treatment option to promote the sustainable use of iron oxides.

The removal of P from agricultural runoff in drainage ditches, using strategically placed filter boxes containing mine drainage derived iron oxides (to serve as the P sorbing material), have been examined by Penn et al. (2007). During their experiments, Penn et al. (2007) noted an additional metal removal capability of acid mine drainage iron oxides, which included observation of the following trace metals being removed from solution: Cu, Zn, As, and Ni.

The idea of using iron oxides as filter media or coatings of sorptive filtration media has developed into a popular area of ongoing research (e.g., Heal et al., 2005; Penn et al., 2007; Wei et al., 2008; Fenton et al., 2009; Sibrell et al., 2009). The application of sorptive filtration technologies to address P pollution is an area of study that Boujelben et al. (2008) have researched in the industrial town of Sfax, Tunisia. Sfax contains a major phosphate manufacturer that has been contributing to high levels of  $\text{PO}_4^{3-}$  contamination in the area's surface waters. Various types of iron oxide coated filter media (including crushed brick, which prior to this experiment was not believed to have been used as a filter media) were examined in batch experiments to determine their effectiveness at removing  $\text{PO}_4^{3-}$  from water. This particular study examined how temperature and pH influenced the P sorption capacities of synthetic iron oxide coated sands, natural iron oxide coated sands, and iron oxide coated crushed brick filter media (Boujelben et al., 2008).

Recovered iron oxides also are being studied to determine the feasibility of using them as a sustainable means of enhancing P removal in constructed wetland treatment processes or as soil

amendments to aid in P removal (Evenson and Nairn, 2000). Heal et al. (2005) conducted research at a tertiary wastewater treatment constructed wetland in Berwickshire, UK that implemented this emerging sorption filtration technology. The objective of their research was to evaluate if the use of iron oxides from recovered mine drainage treatment processes could be successfully applied to reduce the effects of water pollution from eutrophication. Laboratory scale experiments showed that ochre (primarily iron oxides) from a mine drainage treatment system in the UK possessed a phosphorus sorption capacity of up to 26 mg/kg, which effectively removed 90% of P from wastewater effluent after 15 minutes of contact. Heal et al. (2005) concluded that a constructed wetland with an ochre substrate could actively aid in P removal from wastewater effluent for 200 to 300 years. Field scale tests have shown that the current design of their on-site reactor has experienced hydraulic short-circuiting, thus decreasing the P removal capacity.

### Arsenic

Arsenic contaminated groundwater is one of the premier drinking water related human health risks that exists in today's society (WHO, 2001). Highly populated portions of southern Asia such as the Bengal Delta region of Bangladesh and India are among the most severely impacted regions in the world, with estimates of nearly 100 million people at risk of drinking dangerously high levels ( $> 100\mu\text{g/L}$ ) of As contaminated groundwater (Nordstrom, 2002; Smith et al., 2000; Sudipta et al., 2008). Arsenic contamination has been observed to occur naturally in groundwater throughout the world, including the United States. Due to the hydraulic and geologic configuration of the western United States' typically shallow aquifers; they possess an increased risk of As contamination compared to those of the eastern United States (Twarakavi and Kaluarachchi, 2006).

Arsenic has historically been known to be detrimental to human health. Human health effects resulting from the consumption of arsenic laden drinking waters consist of cancer of the skin, bladder, lungs, kidney, liver, and colon (Yu, 2005). Consumption of unsafe As levels ( $> 10 \mu\text{g/L}$ ) in water also can lead to chronic non-cancerous conditions such as diabetes mellitus, and nodular keratosis (Twarakavi and Kaluarachchi, 2006). In effort to avoid the devastating impacts that As can have on global human health, agencies such as the World Health Organization (WHO) and United States Environmental Protection Agency (USEPA) have implemented drinking water maximum contaminant levels (MCLs) in an attempt to monitor and

regulate drinking water sources. Smith et al. (2002) provide a complete chronology of As MCL advancements in the United States, important milestones to date include:

- ❖ 1942 - United States Public Health Service (USPHS) set an interim drinking water standard of 50 µg As/L
- ❖ 1962 - USPHS stated that concentrations above 10 µg As/L should not be used when more suitable supplies are, or can be made available
- ❖ 1975 - US EPA adopted the USPHS 50 µg As/L standard from 1942
- ❖ 1993 - WHO suggested that the US EPA lower its MCL to 10 µg As/L
- ❖ 2001 - US EPA officially adopted 10 µg As/L MCL
- ❖ 2006 - US EPA mandated 10 µg As/L MCL for compliance in January of 2006

Numerous studies have been conducted to examine the sorptive properties that iron oxide coated filter media have for dissolved toxic metals and metalloids such as As (e.g., Fukushi et al., 2004; Thirunavukkarasu et al., 2003; Chakravarty et al., 2002; Manning et al., 1998; Joshi and Chaudhuri, 1996; Webster et al., 1998). Most notably, As has been the focus of these studies due to As arsenic consumption. For example, Katsoyiannis and Zouboulis (2002) and Zeng et al. (2008) have also focused research on removing As from water using sorptive filtration technologies. Between each of these studies, variables such as pH, temperature, As concentration, and flow rate through experimental packed bed filters have been examined to evaluate the sorptive properties and removal efficiency of iron oxides.

Experiments performed by Katsoyiannis and Zouboulis (2002) involving synthetic iron oxide coated polymeric filter media, resulted in low level As (initial concentration 50 – 200 µg/L) removal to residual values below the US EPA primary drinking water MCL of 10 µg As/L. Empirical treatment results from use of synthetic iron oxides, such as the aforementioned study, are promising, thus calling for the need to evaluate the removal capacity of mine drainage derived iron oxides. The possibility of sustainably reusing the vast deposits of mine drainage derived iron oxides in water treatment processes is a concept that potentially contains tremendous benefits for society. The current study examines this precise aspect, in an effort to determine the feasibility of utilizing mine drainage derived iron oxides to treat contaminated waters.

## **Experimental Design & Methods**

### **Point of Zero Charge**

The  $\text{pH}_{\text{pzc}}$  was experimentally calculated in duplicate for the mine drainage derived iron oxides (particle size 75-106  $\mu\text{m}$ ) from Panola Seep #2, Mayer Ranch, and Gowen Battles Seep, as well as for the commercial iron oxide Bayoxide E33 P. The procedure followed for  $\text{pH}_{\text{pzc}}$  determination is based on the static points method described in Ahmed and Maksimov (1968). The method of static points is particularly useful for the analysis of dry oxide powders, in that it makes the equal mass addition of iron to various solutions (of equal volume and different pH) both more convenient and more precise than the addition of amorphous gels (Pechenyuk, 1999). The static-points method was slightly altered for this application by utilizing deionized water instead of an electrolyte solution. This was done in an effort to simulate the low ionic strength conditions existing during the sorption batch experiments.

The revised static-points method is described here for clarification. First, 100 mL of deionized water was individually added to four 300 - mL PYREX glass beakers. Rotary stirrers were then added to each of the containers. The pH of these solutions was then manually adjusted using dilute (0.001M)  $\text{H}_2\text{SO}_4$  and (0.001M) NaOH so that initial pH values of 4.00, 6.00, 8.00 and 10.00 were attained. Next, 0.5000 g of dry iron oxide powder was added to each container and allowed to mix thoroughly. Ahmed and Maksimov (1968) state that equilibrium pH is typically reached within 2 to 6 minutes following the addition of sample to each container. To ensure that an equilibrium pH was obtained, longer reaction times were allotted. An intermediate pH reading was taken after 10 minutes and the final pH was recorded after a 15 minute equilibrium period to verify that the pH had become stable. Once the initial and final pH values are known, the  $\text{pH}_{\text{pzc}}$  can be calculated by determining the number of protons or hydroxyl groups that were sorbed or released by the iron oxide sample. Knowing the surface area of the iron oxide sample allows for the surface charge and surface charge density to be calculated. Plotting the equilibrium pH (x-axis) against the surface charge density (y-axis) yields an x-intercept that indicates the equilibrium pH value at the point where the surface charge equals zero; thus denoting the  $\text{pH}_{\text{pzc}}$  for each sample.

### **Sorption Batch Experiments & Desorption Analysis**

Laboratory scale sorption batch experiments were performed using 500 mL PYREX glass beakers as reaction vessels. Vigorous agitation was supplied by utilizing rotary stirrers and the



pH was held at static values of 6.00, 7.00, 8.00, and 9.00 using Etatron DLXB pH-RX/MBB series combination pH pump/control units. Chemical additions of dilute (0.001M) H<sub>2</sub>SO<sub>4</sub> and (0.001M) NaOH were utilized by the pH control systems to maintain a static pH within ± 0.10 standard pH unit of each set point. Reaction vessels were exposed to ambient laboratory temperatures of 23±1°C during the course of the experiments. Next, 0.1000 g of iron oxide powder (particle size 75-106 µm) from Mayer Ranch passive treatment system, Panola Seep #2, Gowen Battles Seep, and pelletized Bayoxide E33 P were added to separate vessels, each containing contaminant solution volumes of 250 mL per vessel. Initial concentrations of contaminants utilized were approximately 1.0 mg PO<sub>4</sub><sup>3-</sup>/L as KH<sub>2</sub>PO<sub>4</sub> and 100 µg As/L as KH<sub>2</sub>AsO<sub>4</sub>. The ionic strength of each feed solution was calculated for each starting pH and is listed in Table 3. According to Dzombak and Morel (1990), equilibrium is reached relatively quickly when low (< 0.01 mg/mg) sorbate/sorbent ratios are utilized, thus allowing shorter reaction times to suffice. In heed of this general guideline, each iron oxide was allotted 3 hours to reach a state of equilibrium over the pH range 6 to 9. The initial sorbate/sorbent mass ratios used for As and orthophosphate in these experiments were calculated to be 2.5x10<sup>-4</sup> mg/mg and 2.5x10<sup>-3</sup> mg/mg, respectively. Another instance of shorter equilibrium times being used in iron oxide sorption experiments is seen in Sibrell et al. (2009), where a reaction time of 2 hours was used in an experiment examining the sorption of phosphorus onto a mining related iron oxide.

Table 3. Ionic strength of KH<sub>2</sub>AsO<sub>4</sub> and KH<sub>2</sub>PO<sub>4</sub> feed solutions at initial pHs

Feed Solution	Ionic Strength (M)				
	Initial	pH 6	pH 7	pH 8	pH 9
KH <sub>2</sub> PO <sub>4</sub>	4.41E-05	4.46E-05	4.41E-05	4.41E-05	4.41E-05
KH <sub>2</sub> AsO <sub>4</sub>	3.33E-06	3.83E-06	3.38E-06	3.34E-06	3.33E-06

Upon conclusion of these batch reactions, sampling consisted of using sterile syringes to withdraw an adequate sample volume from each reaction vessel and filter it through 0.45µm Millipore nylon filters into 250 mL HDPE bottles (ICP-OES metal analyses), 60 mL HDPE bottles (As analyses), or 125 mL glass Erlenmeyer flasks (orthophosphate analyses). All As samples were then acidified to a pH < 2 with trace metal HNO<sub>3</sub>, preserving the samples for future analysis. Arsenic samples in the 250 mL bottles were analyzed via aqueous microwave digestion/ICP-OES according to EPA methods 3015/6010 in order to examine the desorption of

metals into solution during the As sorption batch experiments (US EPA, 2009). Low level (down to single-digit  $\mu\text{g/L}$ ) As analyses were performed on the samples in the 60 mL bottles via a Perkin-Elmer AAnalyst 800 atomic absorption spectrometer (Norwalk, CT) using a graphite furnace. A five point calibration was constructed prior to Graphite Furnace Atomic Adsorption (GFAA) analysis (Brunson and Sabatini, 2009). The GFAA analysis was performed to determine the As removal that occurred during the sorption batch experiments. Orthophosphate samples (125 mL flasks) were immediately analyzed upon sample collection following Ascorbic Acid Colorimetric Method APHA 4500-P E using a Thermo Scientific Genesys 20 spectrophotometer (APHA, 2005). Additionally, a separate sample was taken from each orthophosphate reaction vessel, passed through a  $0.45\ \mu\text{m}$  Millipore nylon filter (into a 250 mL bottle) and acidified to  $\text{pH} < 2$  with trace metal  $\text{HNO}_3$  to be microwave digested and analyzed on the ICP-OES following EPA methods 3015 and 6010 to check for metal desorption that may have occurred during the orthophosphate sorption batch experiments.

## Results

### Point of Zero Charge

The experiments conducted to estimate the  $\text{pH}_{\text{pzc}}$  for iron oxides evaluated in the sorption batch experiments of this study yielded a range of results. The span of  $\text{pH}_{\text{pzc}}$  results is listed as follows:  $\text{pH}_{\text{pzc}}$  of  $3.21 (\pm 0.35)$  standard deviation) for Panola Seep #2, to  $7.34 (\pm 0.42)$  for Mayer Ranch passive treatment system, respectively. Table 4 provides a complete summary of the  $\text{pH}_{\text{pzc}}$  findings for the iron oxide samples evaluated in the sorption batch experiments.

Table 4.  $\text{pH}_{\text{pzc}}$  values for the three mine drainage derived iron oxides and commercial product examined in the current study (n=2)

Sample Name	Average $\text{pH}_{\text{PZC}}$	Standard Deviation
Mayer Ranch PTS	7.34	$\pm 0.42$
Panola Seep #2	3.21	$\pm 0.35$
Gowen Battles Seep	3.31	$\pm 0.27$
Bayoxide E33 P	6.31	$\pm 0.08$

Graphically, the surface charge density of iron oxide samples from Mayer Ranch, Panola Seep #2, Gowen Battles Seep, and Bayoxide E33 P with respect to equilibrium pH are displayed in Fig. 1-4. Each of these figures show the average data obtained from the duplicate  $\text{pH}_{\text{pzc}}$  runs that were conducted.

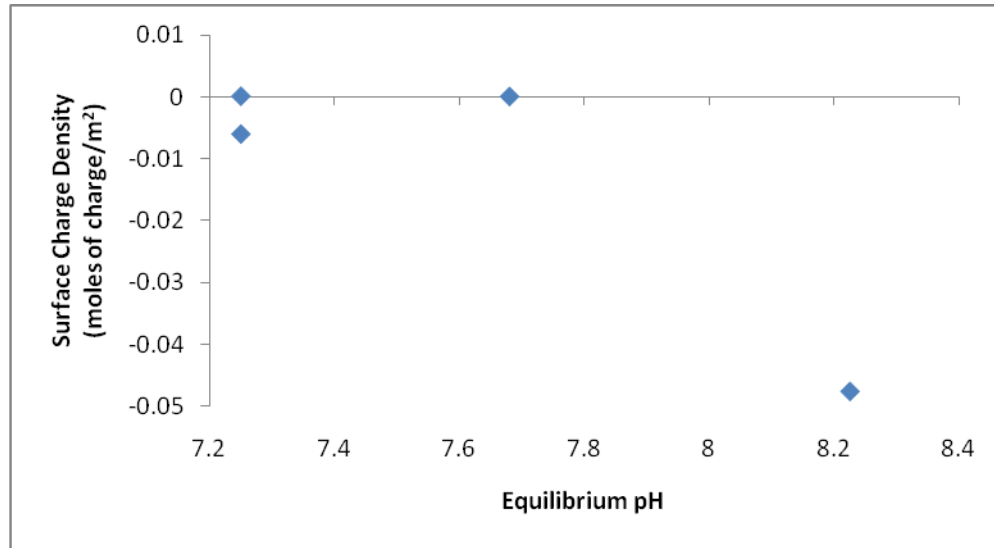


Figure 1. Mayer Ranch passive treatment system surface charge density (moles of charge/m<sup>2</sup>) vs equilibrium pH to determine  $\text{pH}_{\text{pzc}}$

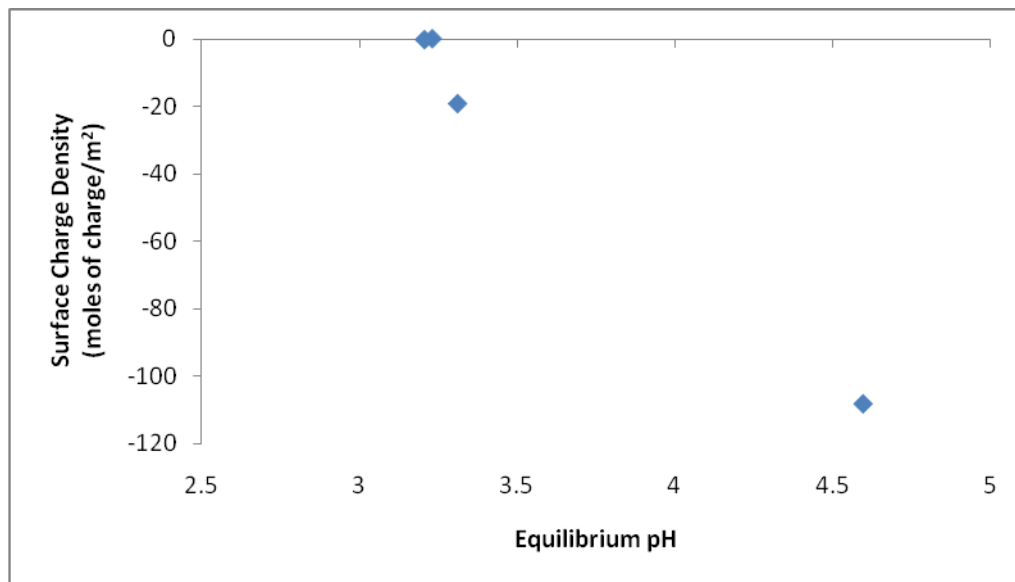


Figure 2. Panola Seep #2 surface charge density (moles of charge/m<sup>2</sup>) vs equilibrium pH to determine  $\text{pH}_{\text{pzc}}$

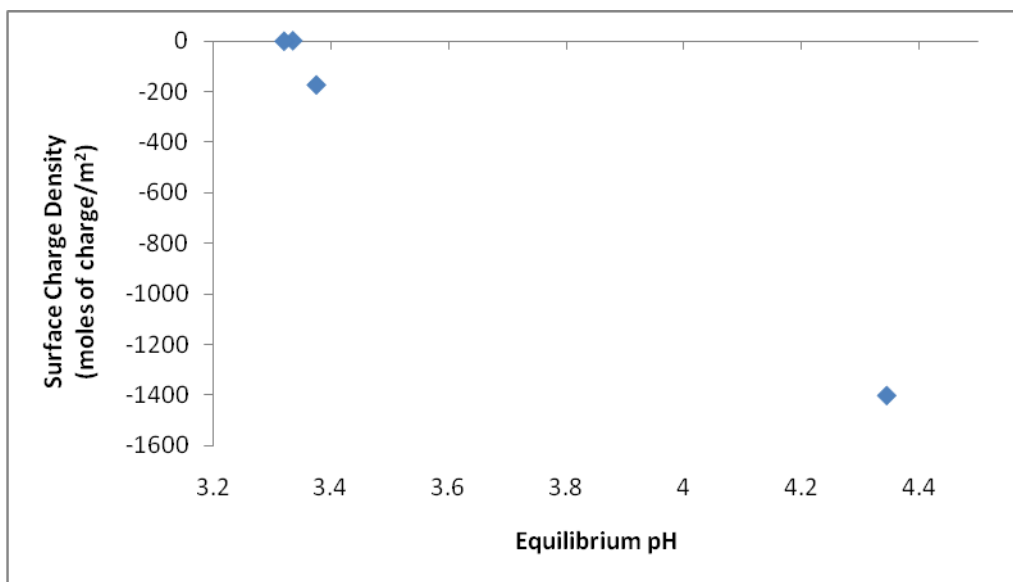


Figure 3. Gowen Battles Seep surface charge (moles of charge/m<sup>2</sup>) vs equilibrium pH to determine pH<sub>pzc</sub>

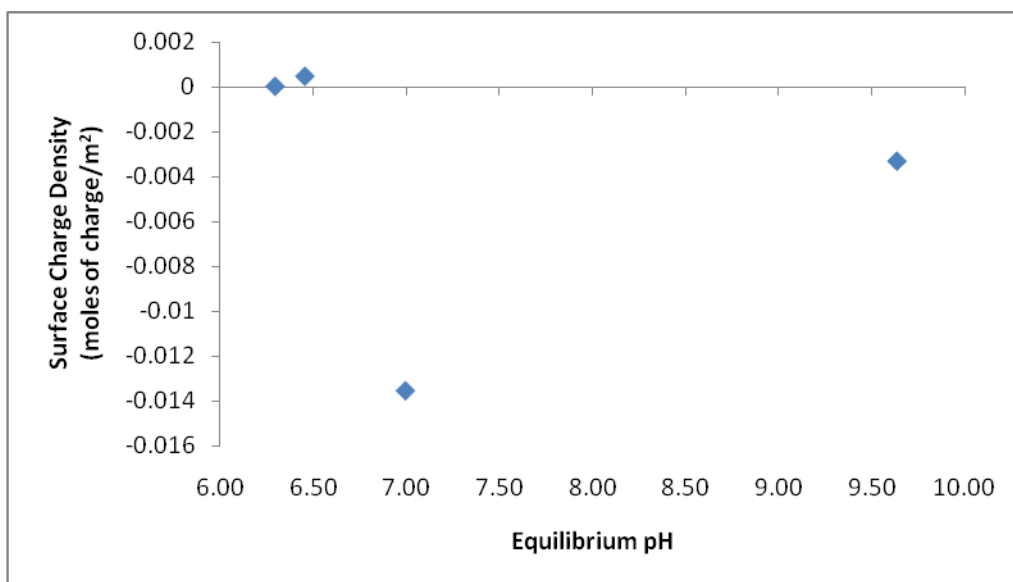


Figure 4. Bayoxide E33 P surface charge density (moles of charge/m<sup>2</sup>) vs equilibrium pH to determine pH<sub>pzc</sub>

### Orthophosphate Sorption Batch Experiments

The orthophosphate sorption batch experiments were performed in triplicate (n=3) for the Mayer ranch system and in five replicates (n=5) for the Battles Seep, Panola Seep #2, and Bayoxide E33 P iron oxide samples. The fraction of orthophosphate removed for each iron oxide is displayed in Fig. 5, 6, 7, and 8 via box and whisker plots, where the top of the box

represents the 3<sup>rd</sup> quartile, bottom of the box signifies the 1<sup>st</sup> quartile, and the middle line represents the median. The differences in orthophosphate removal between the Mayer Ranch and Bayoxide E33 P iron sorbents were statistically significant (assuming a normal distribution of data, all statistical comparisons were justified via a Student's Two Tailed T-Test,  $\alpha = 0.05$ ) at pH 6 and 8, indicating that the Mayer Ranch iron oxide was statistically more efficient at removing orthophosphate than Bayoxide E33 P at these pH values. The differences between observed orthophosphate removal at pH 8 for the Mayer Ranch and Panola Seep #2 iron sorbents were also statistically significant; identifying Mayer Ranch as the more effective sorbent. In comparison to Bayoxide E33 P, Battles Seep possessed a statistically greater performance of orthophosphate removal at pH 6; while Panola Seep #2 was also found to statistically outperform Bayoxide E33 P by exhibiting greater fractions of orthophosphate removal at pH 6 and 7.

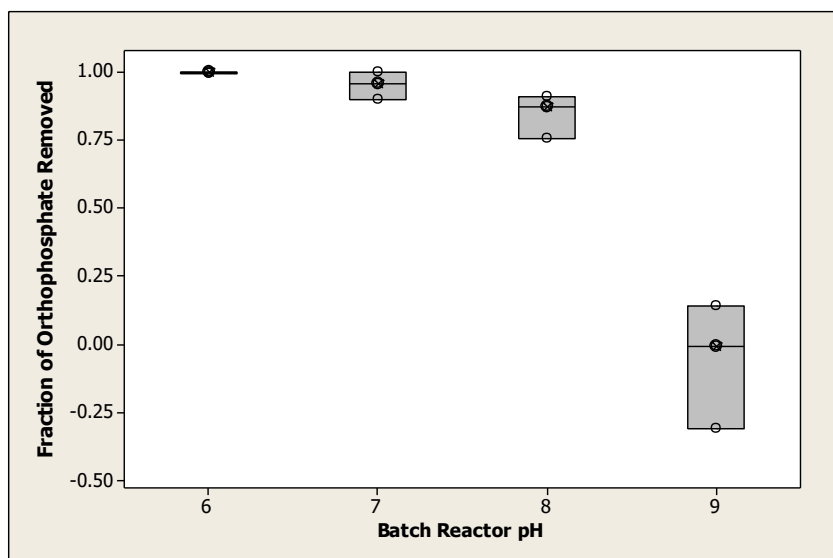


Figure 5. Mayer Ranch iron oxide orthophosphate removal under testing conditions: (0.1000g iron oxide,  $1.13 \pm 0.03$  mg  $\text{PO}_4^{3-}/\text{L}$ ,  $23 \pm 1$  °C, n=3)

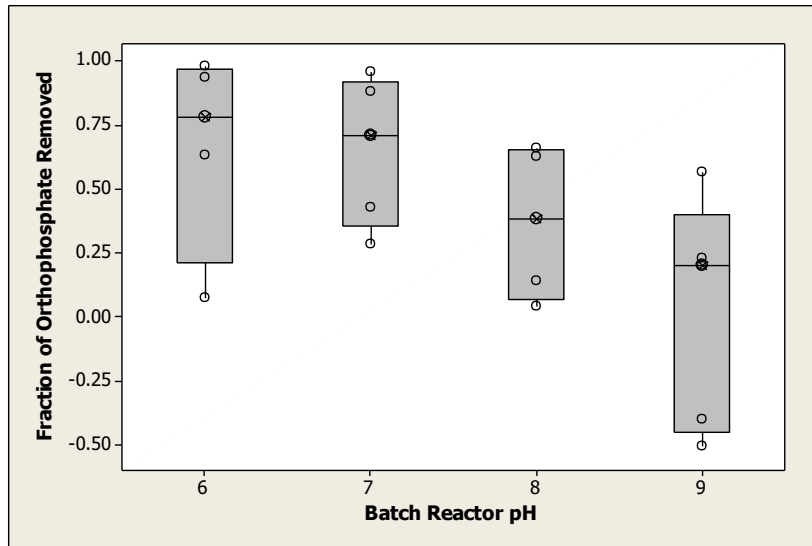


Figure 6. Battles Seep iron oxide orthophosphate removal under testing conditions: (0.1000g iron oxide,  $1.13 \pm 0.03 \text{ mg PO}_4^{3-}/\text{L}$ ,  $23 \pm 1 \text{ }^\circ\text{C}$ , n=5)

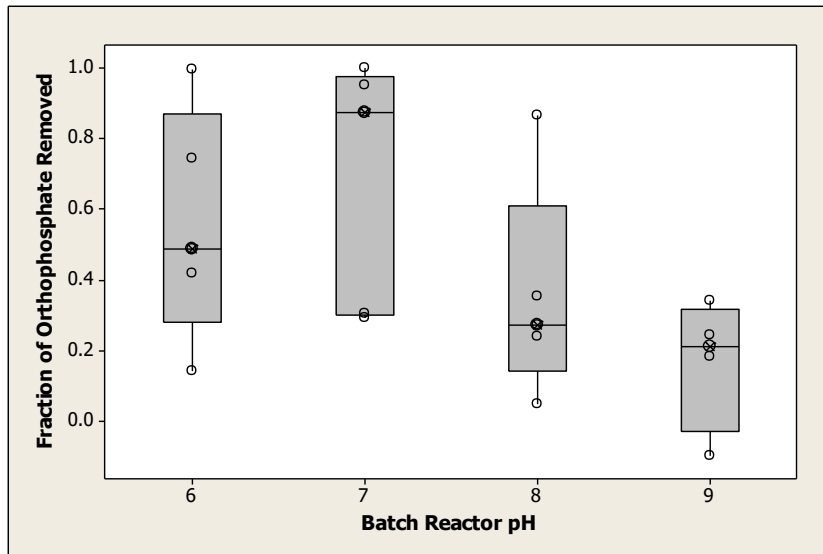


Figure 7. Panola Seep #2 iron oxide orthophosphate removal under testing conditions: (0.1000g iron oxide,  $1.13 \pm 0.03 \text{ mg PO}_4^{3-}/\text{L}$ ,  $23 \pm 1 \text{ }^\circ\text{C}$ , n=5)

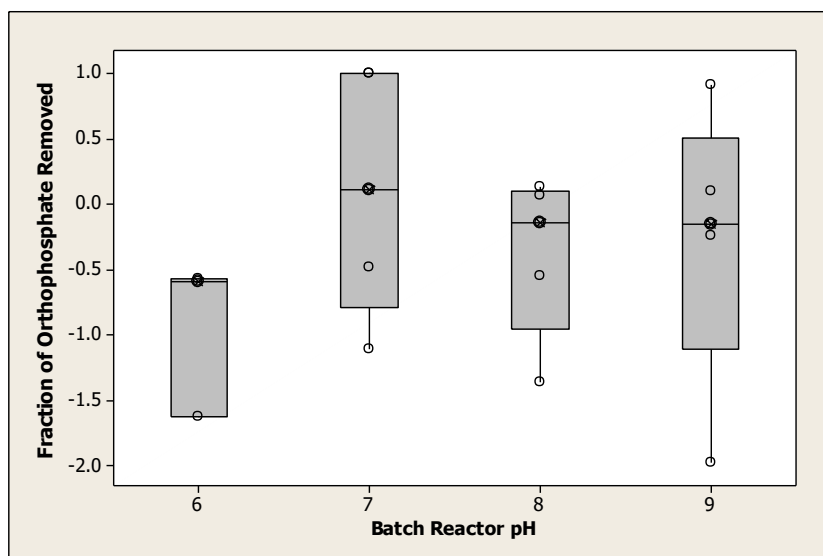


Figure 8. Bayoxide E33 P orthophosphate removal under testing conditions: (0.1000g iron oxide,  $1.13 \pm 0.03$  mg  $\text{PO}_4^{3-}/\text{L}$ ,  $23 \pm 1$  °C, n=5)

The sorption capacity of each iron oxide was determined by calculating how much sorbate ( $\text{PO}_4^{3-}$ ) was removed per 0.1000 g of sorbent (iron oxide) and performing a unit conversion to yield a removal capacity value in mg  $\text{PO}_4^{3-}/\text{kg}$  sorbent. An averaged cumulative graphical representation of this data is presented in Fig. 9. The removal capacity (mg  $\text{PO}_4^{3-}/\text{kg}$  sorbent) of the Mayer Ranch sample was found to be statistically greater than Panola Seep #2 at pH 6 and Bayoxide E33 P at pH 6, 7, and 8. Similarly, Battles Seep proved to have a statistically greater removal capacity at pH 6 and 7 than Bayoxide E33 P, while Panola Seep #2 showed statistically higher removal capacities with respect to Bayoxide E33 P at pH 6, 7, and 8.

In order to portray the overall orthophosphate removal with respect to the mesotrophic treatment goal of between 10 and 30  $\mu\text{g P}/\text{L}$ , a progressive view of orthophosphate concentration from an initial concentration of  $1.13 \pm 0.03$  mg  $\text{PO}_4^{3-}/\text{L}$  versus the equilibrium concentration at each pH value is displayed in Fig. 10. Mayer Ranch clearly distinguishes itself as the only iron oxide sorbent that achieved the mesotrophic orthophosphate removal objective providing an equilibrium  $\text{PO}_4^{3-}$  concentration of 3.1  $\mu\text{g PO}_4^{3-}/\text{L}$  at pH 6 and 53.6  $\mu\text{g PO}_4^{3-}/\text{L}$  at pH 7; which are both below the upper limit of the stated treatment goal. However, the mine drainage derived iron oxide from the Mayer Ranch passive treatment system only exhibits removal to mesotrophic levels at pH 6 and 7.

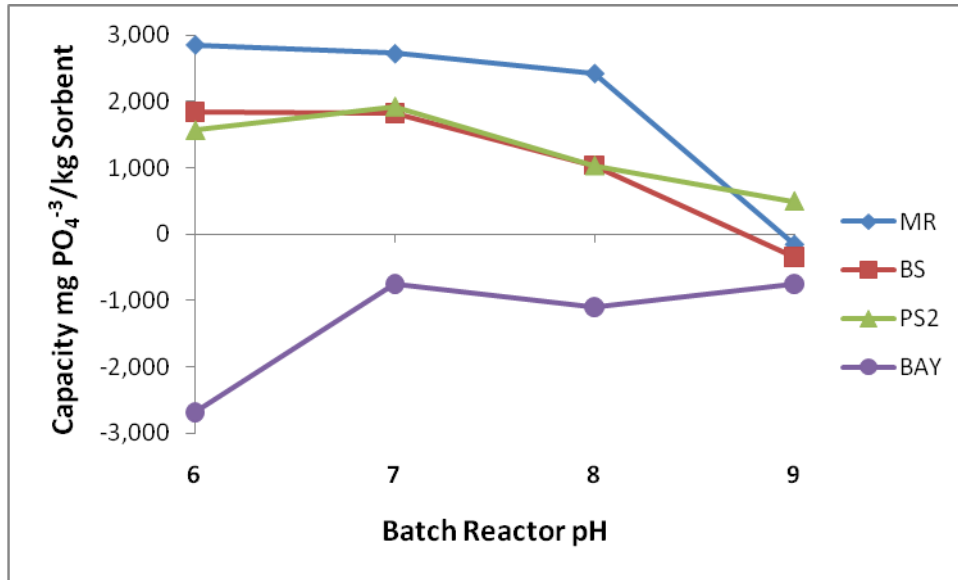


Figure 9. Orthophosphate sorptive capacity vs pH for all iron oxides

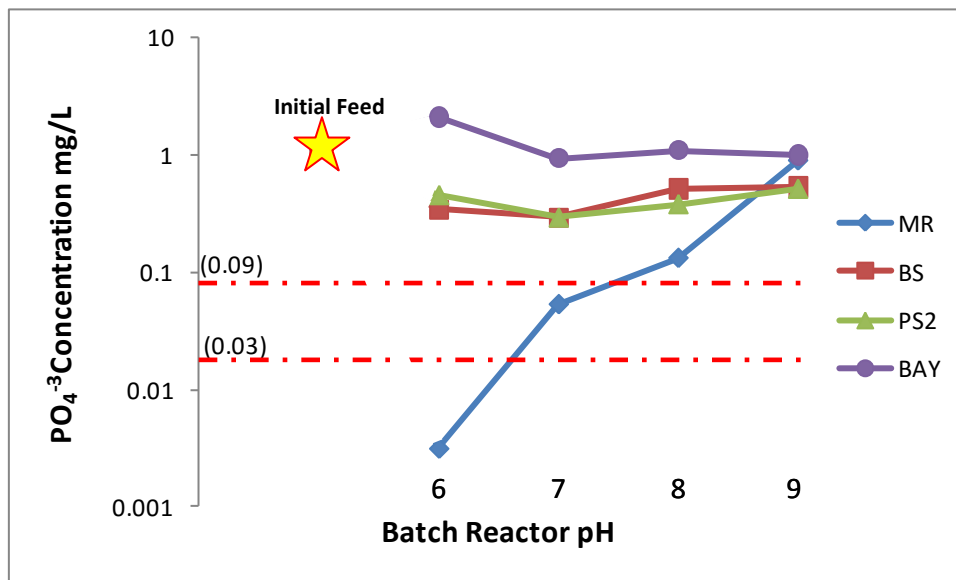


Figure 10. Final orthophosphate concentration with respect to the mesotrophic treatment goal of 0.01 to 0.03 mg P/L [0.03 to 0.09 mg PO<sub>4</sub><sup>3-</sup>/L]; initial conditions: (0.1000g iron oxide, 1.13 ± 0.03 mg PO<sub>4</sub><sup>3-</sup>/L, 23 ± 1 °C, n=5)

### Arsenate Sorption Batch Experiments

The arsenate sorption batch experiments were conducted as a single replicate (n=1). The execution of a single run for each iron oxide at pH values of 6, 7, 8, and 9 were done to provide a general feasibility study of the performance that mine drainage derived iron oxides possess. The percent As removal for each iron oxide is represented in Fig. 11. The preliminary results of mine



drainage derived iron oxides suggest that with the exception of Panola Seep #2 at pH 7, greater than 90 percent removal of As occur at pH values 6 to 8, with a decrease in As removal observed above pH 8. Bayoxide E33 P only showed a significant level of As removal at pH 8, at all other pH values the As removal was at or below a removal efficiency of 25 percent.

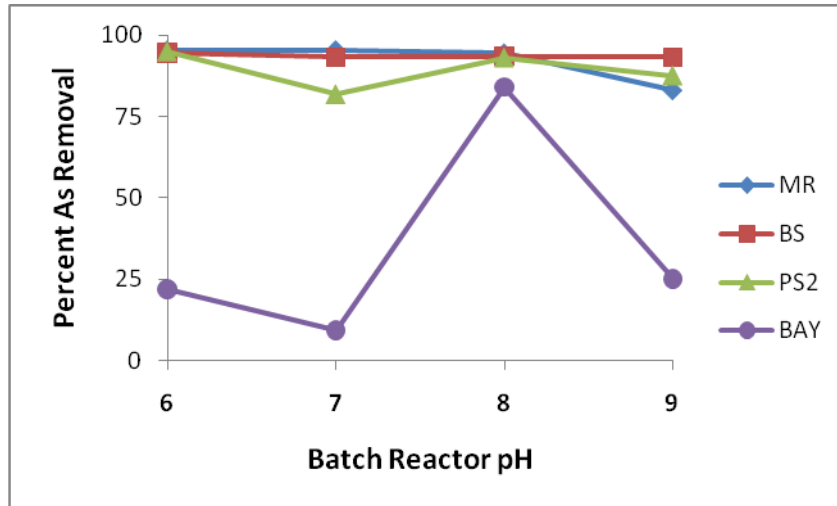


Figure 11. Percent As removal vs pH for all iron oxides (n=1)

The As sorptive capacity (mg As/kg sorbent) for each iron oxide was determined in the same manner as those for orthophosphate. Sorptive capacities for the mine drainage derived iron oxides were found to be as high as 270 mg As/kg at lower pH values and gradually decreased with respect to increasing pH. The highest sorptive capacity for Bayoxide E33 P was observed at pH 8 registering at a value of 226 mg As/kg sorbent. The sorptive capacities of the iron oxides examined in this study are depicted below in Fig. 12.

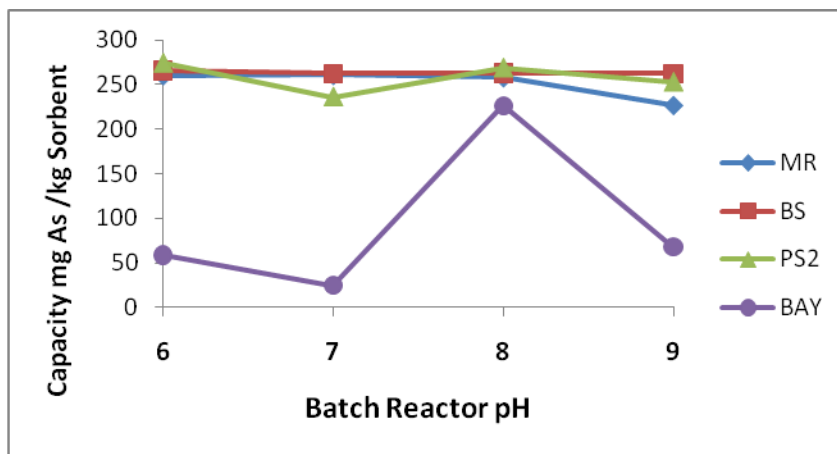


Figure 12. Arsenic sorptive capacity vs pH for all iron oxides (n=1)

The As removal in comparison to the US EPA primary drinking water standard of 10 µg As/L is represented in Fig. 13, with the dashed line illustrating the US EPA primary drinking water standard. Removal of arsenate from an average starting concentration of  $117.79 \pm 4.08$  µg As/L is shown with respect to the static pH at which each batch reactor was held. With the exception of Panola Seep #2 at pH 7 and Mayer Ranch at pH 9, the mine drainage derived iron oxides proved to lower arsenic concentrations to below the US EPA primary drinking water standard. The performance of Bayoxide E33 P approached the US EPA primary drinking water standard at pH 8, with a final concentration of 15.43 µg As/L remaining in solution.

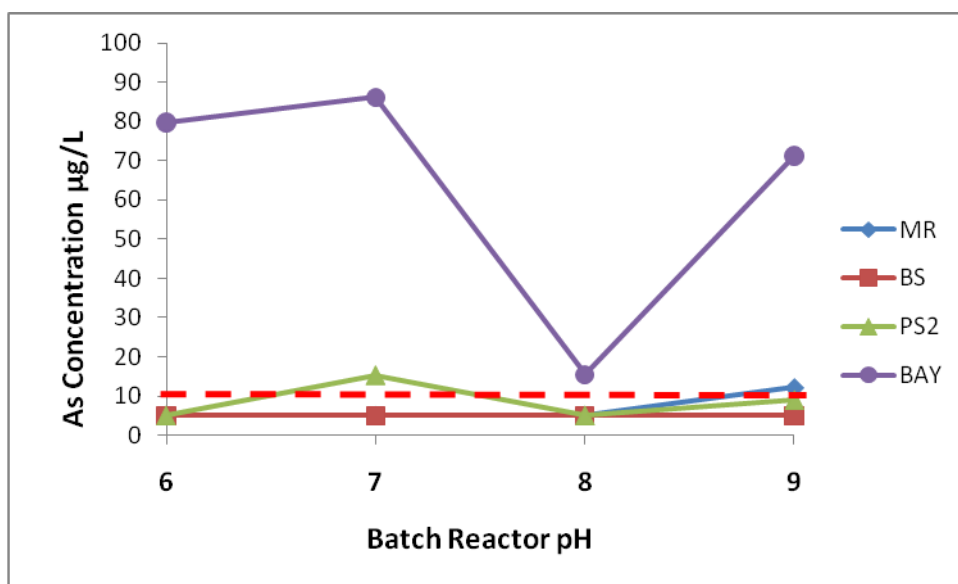


Figure 13. Final arsenic concentration in comparison to the US EPA primary drinking water standard of 10 µg As/L; initial conditions: (0.1000g iron oxide,  $117.79 \pm 4.08$  µg As/L,  $23 \pm 1$  °C, n=1)

### Desorption

Metal desorption from each iron oxide was examined via ICP-OES analysis on samples taken from the batch reactors after 3 hour equilibrium periods with arsenate and orthophosphate. Additionally, Bayoxide E33 P was tested for orthophosphate desorption as a side experiment due to the fact that negative removals were observed at multiple pH values, indicating the occurrence of desorption. Orthophosphate desorption was analyzed by performing an additional run (n=1) of sorption batch reactions at controlled pH values 6, 7, 8, and 9 using 250 mL of deionized water as the feed solution, and analyzing both the deionized water and the solution from each

batch reactor for orthophosphate after a 3 hour equilibrium time. Table 5 shows the amount of  $\text{PO}_4^{3-}$  that was desorbed from the Bayoxide E33 P media following the 3 hour equilibrium period. The extent of orthophosphate desorption observed in Table 5 directly accounts for the magnitude of negative sorptive capacity documented for Bayoxide E33 P in Fig. 9. For example, a unit conversion confirms that at pH 6, 178.41  $\mu\text{g}$  of  $\text{PO}_4^{3-}$  are released into solution per 0.1000 g of sorbent. This relates to a negative sorptive capacity of 1,784.1 mg  $\text{PO}_4^{3-}$ /kg of iron sorbent, which is comparable to the pH 6 sorptive capacity of Bayoxide E33 P displayed in Figure 9.

Metal desorption analyses are an important aspect in determining the potential applicability of reusing mine drainage derived iron oxides in water treatment. No iron oxides were found to desorb metals at concentrations greater than the US EPA primary drinking water standards. Table 6 displays the desorbed metals in solution at the conclusion of the sorption batch experiments in comparison to the primary US EPA drinking water standards. At increased pH (primarily 8 and 9) the mine drainage derived iron oxides exhibited a release of Fe and Al at concentrations exceeding the secondary US EPA drinking water standards. Table 7 lists the desorbed metals for each experiment that were found to be above the secondary US EPA drinking water standards. Note that any pH value that was excluded from Table 7 was found to be less than the drinking water standards, but omitted to simplify the table.

Table 5. Orthophosphate desorption from Bayoxide E33 P ( $\mu\text{g PO}_4^{3-}/\text{L}$ )

	Feed	pH 6	pH 7	pH 8	pH 9
$\text{PO}_4^{3-}$ Concentration ( $\mu\text{g}/\text{L}$ )	< 0.767	178.41	3.06	0.767	< 0.767

Table 6. Metal desorption from iron oxides in comparison to primary US EPA drinking water standards

ID	As(V) Experiment	$\text{PO}_4^{3-}$ Experiment	pH	Regulated Primary Drinking Water Constituents					
				As ( $\mu\text{g}/\text{L}$ )	Cd ( $\mu\text{g}/\text{L}$ )	Cr ( $\mu\text{g}/\text{L}$ )	Cu (mg/L)	Ni ( $\mu\text{g}/\text{L}$ )	Pb ( $\mu\text{g}/\text{L}$ )
MR	X	X	6 – 9	< 5	< 1	< 6	< 0.002	< 10	< 14
BS	X	X	6 – 9	< 5	< 1	< 6	< 0.002	< 10	< 14
PS2	X	X	6 – 9	< 5	< 1	< 6	< 0.002	< 10	< 14
BAY	X	X	6 – 9	< 5	< 1	< 6	< 0.002	< 10	< 14
<b>EPA</b>									
<b>Limit</b>				<b>10</b>	<b>5</b>	<b>100</b>	<b>1.3</b>	<b>100</b>	<b>15</b>

X is a placeholder indicating data is presented for that experiment

Table 7. Metal desorption from iron oxides in comparison to secondary US EPA drinking water standards

ID	As(V) Experiment	PO <sub>4</sub> <sup>-3</sup> Experiment	pH	Secondary Drinking Water Constituents			
				Al (µg/L)	Fe (µg/L)	Mn (µg/L)	Zn (mg/L)
MR		X	9	62	184	1	0.006
BS	X		9	124	474	3	< 0.008
		X	7	55	131	4	0.008
		X	8	132	656	4	0.009
		X	9	231	804	4	0.011
PS2		X	7	27	303	2	< 0.01
		X	8	16	344	2	< 0.01
		X	9	12	407	1	< 0.01
	X		6	6	353	0.4	< 0.008
	X		9	20	363	1	< 0.008
BAY	X	X	6 - 9	< 10	< 280	< 10	< 0.01
<b>EPA Limit</b>				<b>50-200</b>	<b>300</b>	<b>50</b>	<b>5</b>

X is a placeholder indicating data is presented for that experiment

## Discussion

### Point of Zero Charge

The  $pH_{pzc}$  determination for the iron oxides utilized in the orthophosphate and arsenate sorption batch experiments displayed a wide range of  $pH_{pzc}$  values. It was observed that the pH of mine water from which the iron oxide was formed and consequently collected, could influence the relative  $pH_{pzc}$  of mine drainage derived iron oxides. At lower pH values metal dissolution is encouraged, often resulting in higher concentrations of cations in solution that are potentially available for sorption. The sorption of cations to iron oxide surfaces consequently results in the release of protons into solution, thus lowering the  $pH_{pzc}$  of the iron oxide. Conversely, anion sorption is accompanied by proton uptake and an increase in the observed  $pH_{pzc}$  (Dzombak and Morel, 1990). As seen in Table 4, both Panola Seep #2 and Gowen Battles Seep exhibited  $pH_{pzc}$  values in the low 3's which is analogous to the mine water pH (3.08 and 3.70 respectively) in which each was formed. In comparison the Mayer Ranch  $pH_{pzc}$  was noticeably higher in the mid

7's, which originated from a near circum-neutral mine water of approximately pH 6 with considerable net alkalinity.

In comparison to the previous  $\text{pH}_{\text{pzc}}$  values of synthetic goethite which have been reported to range between 7.5 and 9, each sample evaluated in this study was determined to be beneath this documented range (Yates and Healy, 1975; Zeltner and Anderson, 1988). These low  $\text{pH}_{\text{pzc}}$  values could partially be attributed to the fact that atmospheric  $\text{CO}_2$  was not excluded during the pzc determinations. The presence of  $\text{CO}_2$  during these experiments allows for the dissolution of  $\text{CO}_2$  in water, which generates excess protons that contribute in lowering the pH of solution. Interestingly the Mayer Ranch sample was nearest to the  $\text{pH}_{\text{pzc}}$  range of pure goethite even though it contained elevated levels of trace metal such as Zn, Cd, and As previously reported in Neely and Nairn (2010). The presence of impurities associated with the structure and configuration of surface charging is known to influence the point of zero charge possessed by an oxide/hydroxide (Pechenyuk, 1999). Theoretically, cation impurities in an iron oxide would be predicted to lower the  $\text{pH}_{\text{pzc}}$ , yet Mayer Ranch does not follow this logic. A possible explanation for this behavior could be the incorporation of the metal species as inner sphere complexes, thus allowing the surface sites to still be occupied by a high number of protons contributing to a relatively high  $\text{pH}_{\text{pzc}}$ .

Mayer Ranch passive treatment system and Bayoxide E33 P both exhibit relatively low surface charge density values. Mayer Ranch exhibits a nearly neutral surface charge between pH 7.25 and 7.70. Bayoxide E33 P also displayed the unique trend of  $\text{pH}_{\text{pzc}}$  where the overall charge stayed near neutral over an extended range of pH values as seen in Fig. 4. Since Bayoxide E33 P is a commercial product, it is likely that the charge density was optimized in the design phase to encourage sorption over broad pH ranges.

### Sorption of Orthophosphate

Upon evaluation of each mine drainage derived iron oxides' performance at removing orthophosphate from solution, the most striking observation was the large variation in total removal that existed between replicates at each pH. This large degree of intrinsic variation can be seen by the large range that exists between the 1<sup>st</sup> and 3<sup>rd</sup> quartiles in the box and whisker plots previously provided. The use of Dixon's Q test was performed on individual points to determine if they could be statistically classified as outliers within the dataset. Due to the

relatively small sample size ( $n=5$ ), only 3 outliers were identified within the entire orthophosphate experimental dataset. The outliers identified via the Dixon's Q test were justifiably excluded from the dataset in effort to more accurately portray the data in a manner that minimized the experimental variation.

Natural variation due to sample heterogeneity is believed to account for the deviations observed in replicate experimental runs. To compound this, small masses of iron were used for each of these experiments (0.1000 g). The use of such small sample sizes would magnify any error that exists due to the heterogeneous nature of the mine drainage derived iron oxide samples. Additionally, little is known of the exact configuration of inner sphere or outer sphere complexes for these field-derived sorbents, making it difficult to project the availability of remaining sorption sites.

The Mayer Ranch iron oxides were collected from concrete sluice-ways that carry the water from the discharge points to the oxidation pond. Although overlooked at the time of collection, sampling from these structures ensured a higher sample integrity consisting primarily of the iron precipitates. The unintentional clay and silica contamination that was likely present at the other locations was effectively avoided at Mayer Ranch due to these structures. This detail helps to explain why the errors seen between Mayer Ranch samples were so small in comparison to the other locations. The sampling locations of Gowen Battle Seep and Panola Seep #2 both exist as environmental discharges where the base soil likely contained both silica and clay. This suggestion is supported by the high Al content of the iron precipitates from these locations ( $MR < PS2 < BS$ ) as shown in Neely and Nairn (2010). Additionally, it is worth noting that characteristic XRD peaks of various clays and quartz were observed to exist in most of the samples, showing increased intensity counts for Battles Seep, Leboskey, Panola Seep #2, GCI, and Gowen Confluence (additional mine drainage derived iron oxides analyzed in the previously mentioned Neely and Nairn 2010 study).

The presence of silicate clays has been shown to increase P desorption, especially in the presence of aqueous Al and other multivalent cations that have strong affinities for P binding sites (Shariatmadari and Mermut, 1999). Aside from the differences in surface area ( $MR > PS2 > BS$ ) the presence of clay in the iron samples and its subsequent tendency to desorb P could account for the slightly lower removal capabilities of Battles Seep and Panola Seep #2 in

comparison to Mayer Ranch. The sorption batch experiments did not contain aqueous Al in the feed solutions, but at each pH value trace amounts of Al and other cations were detected by ICP-OES analysis. The detection of these constituents suggests that a limited amount of desorption from the iron oxides occurred, making the slight desorption of orthophosphate a possibility. However, if any orthophosphate were desorbed from the mine drainage derived iron oxides, it only slightly decreased the overall orthophosphate removal efficiency as relatively high net removals were still observed for all mine drainage derived iron oxides. Yet this seems to be a likely explanation for the lower orthophosphate removals observed with Battles Seep and Panola Seep #2 in comparison to Mayer Ranch.

Another location-based factor that could influence the orthophosphate sorption capability of Battles Seep is the fact that it exists in an open field that the landowner uses as a cattle loafing area. This land use potentially introduces agricultural runoff with elevated P concentrations into the drainage ditch that transports the mine water. It seems possible that the Fe accumulating at this location could already have orthophosphate incorporated into its solid structure through substitution processes. However, it is more likely that the orthophosphate would exist as a surface complex, bound to the iron oxide particles. During the sorption experiments no net orthophosphate desorption was noted for the Battles Seep sample, suggesting that if any orthophosphate is contained as surface complexes on these Fe particles, it likely exists as inner sphere complexes that are held together by stronger bidentate bonds as opposed to the weaker monodentate bonds associated with many outer sphere complexes (Atkinson et al., 1972; Ghosh et al., 2006).

The general trend of anion removal with respect to increasing pH is: that above the  $pH_{pzc}$  of a sorbent the removal efficiency gradually decreases (Dzombak and Morel, 1990). With the exception of Bayoxide E33 P, this typical trend was observed for all iron oxides tested in this study ( $PO_4^{3-}$  removal  $pH\ 6 > pH\ 7 > pH\ 8 > pH\ 9$ ). The maximum orthophosphate sorptive capacity of the mine drainage derived iron oxides were found to occur at pH 6: Mayer Ranch ( $2,850 \pm 90\ mg\ PO_4^{3-}/kg$ ); Battles Seep ( $1,840 \pm 1,180\ mg\ PO_4^{3-}/kg$ ); Panola Seep #2 ( $1,570 \pm 890\ mg\ PO_4^{3-}/kg$ ). Previous studies have reported phosphorus sorptive capacities [expressed as orthophosphate sorptive capacities for comparison purposes in brackets] for mining related iron oxides and are listed as follows:  $26\ mg\ P/kg$  [ $79\ mg\ PO_4^{3-}/kg$ ] (Heal et al., 2005);  $16 - 21\ g\ P/kg$  [ $49,079 - 64,417\ mg\ PO_4^{3-}/kg$ ] (Fenton et al., 2009);  $1,540 \pm 40\ mg\ P/kg$  [ $4,723 \pm 122\ mg$

$\text{PO}_4^{3-}/\text{kg}$ ] (Evenson and Nairn, 2000); 1,820 – 23,900 mg P/kg [5,582 – 73,312 mg  $\text{PO}_4^{3-}/\text{kg}$ ] (Sibrell et al., 2009). In comparison to these previous findings, it appears that the orthophosphate sorptive capacities of the mine drainage derived iron oxides examined in this study are comparable, with the exceptions of the higher values in the range documented by Sibrell et al. (2009) and the full range of reported values by Fenton et al. (2009).

A multitude of factors likely contribute to the observed differences in sorption capacity of the current study when compared to published results of previous research experiments. An important aspect to note is that the pH of solution was not controlled in any of the previously cited studies. As a result, higher sorption capacities likely were observed in their experiments, especially if conducted at low pH. Another fundamental difference impacting the sorption capacities between iron oxides of the current study and those previously performed is the initial concentration of contaminants. The low contaminant concentrations used in the sorption experiments may have contributed to the comparatively low sorption capacities observed with respect to the higher range values presented by Fenton et al. (2009) and Sibrell et al. (2009). Also, the Sibrell et al. (2009) sorptive capacities were determined via the Freundlich adsorption isotherm expression, while Fenton et al. (2009) used the Langmuir adsorption isotherm expression. Dependent upon how closely the different isotherm assumptions apply to a specific iron oxide sorbent, the resulting accuracy of calculated sorptive capacities will likely vary.

#### Sorption of Arsenate

The feasibility of using mine drainage derived iron oxides to remove arsenic from drinking water was supported by a single experimental run where the removal of As below the primary US EPA drinking water standard of 10  $\mu\text{g}/\text{L}$  was observed between pH 6 and 9. The only instances where the As drinking water standard was not met with mine drainage derived iron oxides occurred at Mayer Ranch pH 9 (12.17  $\mu\text{g}/\text{L}$ ) and Panola Seep #2 pH 7 (15.27  $\mu\text{g}/\text{L}$ ). Based on this limited information, it appears that mine drainage derived iron oxides are capable of treating arsenate contaminated drinking water sources to US EPA standards. However, further examination and testing of these iron oxides are required before the validity of this application can be stated definitively.

Interestingly, the arsenic specific commercial iron oxide media Bayoxide E33 P did not perform as expected. Bayoxide E33 P is advertised by Severn Trent Services to treat As



contaminated water to below 10 µg/L. In this particular experiment, the lowest final concentration of arsenic contaminated water treated by Bayoxide E33 P was 15.43 µg/L at pH 8, which still exceeds the US EPA primary drinking water standard. A contributing factor that helps explain the observed increase in As removal at pH 8 is due to the variation in As speciation that occurs with respect to oxidizing conditions and pH. As the charge of arsenate species rise with respect to increasing pH; an optimum arsenate removal condition near pH 8 has been identified in pilot scale As removal plants utilizing Bayoxide E33 P media (STS, 2007). Similarly, this removal ‘sweet spot’ was documented in the current study and is illustrated in Fig. 11 and 12. Although an optimal pH of 8 did yield an increased arsenic removal; the resultant concentration did not meet the US EPA primary drinking water standard of 10 µg/L for As. The material safety data sheet for Bayoxide E33 P explicitly states that it should not be used to treat waters above pH 10 or below pH 5. The pH range used during the arsenate sorption experiment (pH 6 - 9) stayed within the manufacturer’s specifications, yet decreases in performance still were observed.

A possible explanation for the poor performance of Bayoxide E33 P observed in the arsenate sorption batch experiments involves the details of the experimental design. The issue alluded to deals with the constant agitation applied to the reaction vessels by rotary stirrers. Bayoxide E33 P is not specifically designed for such conditions; it is traditionally used as a packed bed filter media that would typically experience more uniform and unidirectional flows. Consequently in some instances the rotary stirrers were observed to contact settled Bayoxide media, breaking apart the pellets. The existence of structurally compromised media could account for decreased performances exhibited by Bayoxide E33 P. However, this explanation seems unlikely due to the fact that there would not be a significant change in the surface area of compromised grains of media because the majority of the surface area exists as internal features of the Bayoxide E33 P media. Additionally, the poor performance of Bayoxide E33 P media could be attributed to its intrinsic sorption kinetics. It is possible that the time provided may not have been adequate for Bayoxide E33 P to reach a state of equilibrium during the sorption experiments. Since the particle size of Bayoxide E33 P (0.5 – 2.0 mm) is effectively 100 times larger than the mine drainage derived iron oxides (75 – 106 µm) and nearly 99.9% of its surface area is internal, its diffusion based sorption kinetics would be significantly slowed when compared to the sorption kinetics of the mine drainage derived iron oxides.

## Desorption

The ICP-OES analysis of metals desorbed in the As and phosphate sorption tests showed that none of the iron oxides examined in this study desorbed metals in excess of the primary US EPA drinking water standards. However, all of the mine drainage derived iron oxides exhibited some level of either Fe or Al that was above the secondary US EPA drinking water standards. The secondary US EPA drinking water standards are not federally enforceable, yet many states opt to enforce them at the state level to help control the aesthetic qualities of water such as taste, odor, and color. As seen in Table 7 the higher pH values of 8 and 9 were associated with a higher occurrence of Fe and Al levels. The Fe and Al in solution might have been present as colloidal particles of iron oxide or clay that may have passed through the 0.45  $\mu\text{m}$  filters used to separate the solids from solution at the end of each batch experiment. Thus, measured concentrations might not be representative of truly dissolved constituents.

During the orthophosphate test runs (n=5) for Bayoxide E33 P net desorption was observed at nearly all pH values. In order to confirm that orthophosphate was coming from the Bayoxide E33 P media, a blank run with deionized water as the feed solution was performed. Upon analysis of this run it was confirmed that orthophosphate was being released from the Bayoxide media. The orthophosphate concentration for the deionized water feed solution was below the detection limit of the ascorbic acid colorimetric test. Yet the solutions containing Bayoxide E33 P contained orthophosphate at pH 6, 7, and 8 as shown in Table 5. In fact, the orthophosphate concentration of 178.41  $\mu\text{g/L}$  at pH 6 is already above the mesotrophic treatment goal for fresh waters, showing how poorly the As specific Bayoxide E33 P performs as an orthophosphate sorbent.

Alternatively, Bayoxide E33 P proved to have optimum performance with respect to metal desorption. The Bayoxide media was below all primary and secondary US EPA drinking water limits. This result likely is due to a combination of lower concentrations of metal impurities found in Bayoxide E33 P media as well as the pelletized homogeneous nature of the media. The discrepancy in particle size between the larger Bayoxide E33 P pellets and the smaller mine drainage derived iron oxide powders also helps to explain how even the broken Bayoxide E33 P pellets may have remained large enough to be removed almost entirely by the 0.45  $\mu\text{m}$  filters used in sample preparation.

## Conclusions

Overall, the sorption batch experiments for orthophosphate and arsenate showed that mine drainage derived iron oxides possess the capability of treating naturally occurring levels of As and P contaminated waters. The mine drainage derived iron oxides evaluated in this study did not release any dissolved metals into solution at concentrations that were above the primary US EPA drinking water standards. With respect to orthophosphate removal the large degree of variability and possible inclusion of silicate clay contamination in the composition of iron precipitates from Gowen Battles Seep and Panola Seep #2 decreased their performance compared to iron oxide from Mayer Ranch passive treatment system. The Fe from Mayer Ranch (at pH 6 and pH 7) was the only sorbent that removed orthophosphate below the mesotrophic treatment goal. Despite the variability in mine drainage derived iron oxide composition, their As removal efficiencies were observed to occur at impressive levels. With the exception of Mayer Ranch (pH 9) and Panola Seep #2 (pH 7); a single experimental run showed As removals were below the primary US EPA drinking water standard of 10 µg/L. Thus indicating that it may be feasible to beneficially re-use mine drainage derived iron oxides to treat As contaminated drinking water sources.

In comparison to Bayoxide E33 P, the mine drainage derived iron oxides performed better across the entire testing spectrum with respect to contaminant removal. Although water treated with Bayoxide E33 P conformed to all of the secondary US EPA drinking water standards, the Mayer Ranch, Battles Seep, and Panola Seep #2 exceeded the Fe and/or Al secondary drinking water standards at pH 8 and 9.

Future research on this topic is needed to verify the performance of mine drainage derived iron oxides for the removal of both orthophosphate and arsenate. Additional iron oxides also should be tested through sorption experiments to determine if they possess similar capacities for the sorption of orthophosphate and arsenate. Further studies also should be performed to explore the feasibility of using mine drainage derived iron oxides for cation removal applications. Beyond further replication, examining additional iron oxide samples, and evaluating other contaminants, the next step in verifying the application of mine drainage derived iron oxides in water treatment is to assess the sorption kinetics. Additionally, the development a filter prototype for either laboratory or pilot scale testing is needed to evaluate performance on a larger scale.

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