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Sulfate Removal from Water

Ashref Darbi,[1] Thiruvenkatachari Viraraghavan,[1]*
Yee-Chung Jin,[1] Larry Braul[2] and Darrell Corkal[3]

[1]*Faculty of Engineering, University of Regina, Regina, Saskatchewan S4S 0A2*
[2]*Agriculture and Agri-Food Canada, Regina, Saskatchewan*
[3]*Agriculture and Agri-Food Canada, Saskatoon, Saskatchewan*

Sulfate occurs naturally in groundwater. Concerns regarding the health effects from sulfate in drinking water have been raised because of reports that diarrhea may be associated with water that contains high levels of sulfate. In the livestock production industry, there is a concern that high levels of sulfate in water can adversely affect productivity. Different methods can be used to remove sulfate from water. Proven technologies are ion-exchange, nanofiltration, reverse osmosis, and electrodialysis. A few earlier studies have shown that the use of bentonite/kaolinite for sulfate removal has produced encouraging results. Experimental work was undertaken to examine in detail the feasibility of such processes. Laboratory studies using bentonite showed poor or no removal in the case of high sulfate water. Ion exchange and nanofiltration were found to be very effective in removing sulfate. Ion exchange is likely to be more reliable than nanofiltration because of the sensitivity of the nanofiltration process to total dissolved solids and biofouling.

Key words: **sulfate removal, drinking water, bentonite, ion exchange, nanofiltration**

Introduction

Sulfate occurs naturally in groundwater. Sulfate ions present in water in high concentrations may cause temporary and acute effects on humans and animals, including diarrhea. The United States Environmental Protection Agency (U.S. EPA) has proposed a maximum allowable concentration of 500 mg/L for sulfate in drinking water in order to avoid any health concern regarding human consumption. A secondary maximum allowable concentration for sulfate has been set at 250 mg/L (U.S. EPA 1994).

It is understood that approximately 30% of groundwater in Saskatchewan exceeds a sulfate concentration of 1000 mg/L (Shaheen and Sketchell 1998), the maximum objective level for livestock watering set by the Saskatchewan Environment and Resource Management. In some cases, sulfate concentrations are reported to be as high as 3000 mg/L. It is believed that the removal of sulfates from drinking water will lead to a healthier livestock and a more productive herd. On the other hand, sulfate

* Corresponding author; t.viraraghavan@uregina.ca

is a necessary constituent in the bodies of humans and other animals. In humans, serum sulfate levels range from 24 to 36.5 mg/L. Sulfate is involved in many biochemical activities including the production of chondroitin sulfate and sulfation of exogenous chemicals.

Three cases from Saskatchewan were reported with infants experiencing gastroenteritis with diarrhea and dehydration upon ingesting water that had high levels of sulfate (650–1150 mg/L) (Chien et al. 1968). Diarrhea subsided in all infants when different water sources with lower sulfate concentrations were used (Backer 2000). Members of an expert workshop on sulfate concluded that there was not enough scientific evidence to support a regulation creating a Maximum Contaminant Level (MCL) for sulfate in drinking water (Backer et al. 2001).

In the livestock production industry, there is a concern that high levels of sulfate in drinking water can adversely affect productivity. A study conducted by Veenhuizen et al. (1992) on nursery pigs given drinking water containing sodium or magnesium sulfate at 600, 1200, and 1800 mg/L of sulfate for 28 days, showed that pigs drinking high sulfate water had a higher frequency of non-pathogenic diarrhea than the controls (i.e., pigs drinking water with 54 mg/L naturally occurring sulfate) (Backer 2000). It also showed that sulfate levels in excess of 500 mg/L can cause laxative effects on young animals, with cattle becoming more resistant within several weeks (J. Cory, Prairie Farm Rehabilitation Administration, Regina, Sask., pers. comm.). Levels of sulfate greater than 300 to 600 mg/L can cause chronic diarrhea, electrolyte imbalance, and possible death.

Different treatment technologies have been investigated for sulfate removal. Proven technologies for the removal of sulfate from drinking water include ion exchange, nanofiltration, reverse osmosis and electrodialysis (Table 1). In addition, several studies have been reported on the use of bentonite/kaolinite adsorption for sulfate removal. While such

Table 1. Different sulfate removal technologies (Marhaba and Washington 1997)

Treatment technology	Description
Reverse osmosis/nanofiltration	Water is forced under pressure through a porous membrane designed to remove ions from the water
Ion exchange	Inorganics are removed by passing water over cation and anion exchangers, replacing cations and anions with H^+ or Cl^- or OH^-
Electrodialysis	Direct current is applied across a body of water separated into vertical layers alternatively permeable to cations and anions

studies have reported mixed results, an optimized system based on bentonite adsorption would have a significant economic advantage over the other technologies.

A study conducted by Rao and Sridharan (1984) on the adsorption of sulfate by kaolinite found that sulfate was adsorbed at positive and neutral sites with the displacement of OH_2 and OH^- groups. Adsorption of sulfate occurred significantly at positive sites at low concentrations whereas on increasing the solution concentration, the proportion of sulfate adsorption at the neutral site increased. The level of positive charge on the clay surface apparently governs the form of surface bonding. At low anion saturation, sulfate was adsorbed on kaolinite as a divalent ion. At a higher solution concentration, the surface favours the adsorption of the monovalent ions and thus sulfates formed are in both monodentate and bidentate complexes.

The objectives of this study were to examine in detail the feasibility of using bentonite to remove sulfate from groundwater; and to compare sulfate removal using bentonite with ion exchange and nanofiltration processes.

Materials and Methods

The removal of sulfate from water was investigated using various treatment methods. Removal of sulfate through adsorption was examined using different concentrations of bentonite. Three types of test water (tap water spiked with sulfate, and groundwater from Leroy and Swift Current in Saskatchewan) were used in the experiments. Sulfate-spiked tap water was prepared by weighing a known amount of calcium sulfate or magnesium sulfate and adding this amount to the tap water to obtain the desired sulfate concentration. Final sulfate concentrations were measured by Dionex before starting the experiments. Groundwater samples from Leroy and Swift Current were collected by the Prairie Farm Rehabilitation Administration (PFRA) in February 2001, transported to the University of Regina in an open van and stored in a refrigerator at 4°C. All adsorption experiments with bentonite were repeated three times using tap water spiked with sulfate. In addition, ion exchange and nanofiltration techniques were investigated to examine the removal capabilities through these systems. Ion exchange and nanofiltration experiments were repeated three times for each water type used. Duplicate samples were collected for each analysis. Average values were used in data analysis. The characteristics of groundwater samples from Leroy and Swift Current provided by PFRA are shown in Table 2.

Adsorption of Sulfate to Bentonite

Sulfate adsorption studies were conducted under different bentonite concentrations. Bentonite was obtained from Canadian Clay Products, Wilcox, Saskatchewan. Different concentrations of sulfate

Table 2. Characteristics of water samples

Sample	pH	Cl^- (mg/L)	NO_3^--N (mg/L)	SO_4^{--} (mg/L)	Hardness (mg/L as $CaCO_3$)	Conductivity µS/cm	TDS (mg/L)
Tap water	7.5	18	0	185–200	232	534	230
Leroy (groundwater)	7.2	295	15	2280	2735	—	3750
Swift Current (groundwater)	7.7	112	18	3665	3700	6200	—

were used in the study. Calcium sulfate was dissolved using tap water. Batch isotherm studies with bentonite concentrations of 400, 500, 600, 700, 800, 900, and 1000 mg/L were performed at 23 ± 1°C. Bentonite was weighed and placed in 250-mL Erlenmeyer flasks. The flasks were then filled to 100 mL with calcium sulfate solution and covered with parafilm wax. The mixtures were placed in a gyratory shaker, at 200 rpm, for 15, 30, 45, 60, 75, 90, 115, 120, 180, and 240 minutes. pH values were measured prior to, and at the end of the contact period, using a Hanna model 1024 pH meter. At the end of each contact time, the bottle reactor was removed and 40 mL of the mixture was decanted into a centrifuge tube for analysis. The mixture was centrifuged for 15 minutes at 6000 rpm to separate the bentonite from the solution. The supernatant was diluted 1:10 with distilled water and analyzed for sulfate using a Dionex Ion Chromatograph.

Sulfate Removal by Ion Exchange

Column experiments were conducted to examine sulfate removal by an anion exchange resin. A high capacity, type 2 ionic resin (ASB 2) was used for all column experiments (Sybron Chemicals Inc., Birmingham, New Jersey). Bead size distribution of the ionic resin ranged between 0.3 to 1.2 mm with a particle density of approximately 1.11 g/mL. Total exchange capacity, as $CaCO_3$, was 1.4 eq/L or 30.6 kg/ft^3. Water content of the ASB 2 resin was between 38 and 45%.

The column apparatus consisted of an acrylic column, 90 cm long and 1 cm internal diameter (ID) with two butyl rubber stoppers used as end caps. The resin was packed to a height of 80 cm. The end caps were machined with a small hole, 0.64 cm in diameter, to allow for influent and effluent discharge. A glass filter was placed above the bottom end cap to prevent resins from leaving the column. Silicon tubing (Nalgene) was used to connect the input reservoir to the column. The effective volume packing was measured gravimetrically for each individual packing. Tap

water spiked with sulfate and Leroy and Swift Current groundwater were used in ion exchange column experiments.

The column was flooded with 20 L of tap water containing 1000 mg/L of sulfate, using a peristaltic pump (Cole Parmer). Magnesium sulfate was used instead of calcium sulfate because a high concentration of calcium sulfate will cause a high-turbidity solution. High-turbidity water will form scale on the membrane and affect the capacity of the resin. Saturation of the column was achieved by a down-flow gradient of 75 mL/min, which maintained a constant head of 1 cm above the anion resin. The effluent was collected in scintillation vials after the first 60 min and every 30 min thereafter for 4 h, when breakthrough was observed.

Nanofiltration

Nanofiltration is a pressure-driven membrane process with performance characteristics between reverse osmosis and ultrafiltration. The theoretical pore size of the membrane is 1 nm. A nanofiltration unit was obtained from Water Group with Filmtec 2.5" nanofiltration elements, model NF 90-1812-HF. The unit was designed for home use and small production.

Spiked tap water using magnesium sulfate with different initial concentrations was used at two different pressures of 40 and 80 psi. Initial concentrations varying from 916 to 5363 mg/L were used in the runs. Sampling was conducted during the initial, intermediate, and final stages of the experimental procedure. Groundwater samples from Leroy and Swift Current were also examined using nanofiltration.

Results and Discussion

Sulfate Adsorption to Bentonite

Figure 1 illustrates the concentration of sulfate using different bentonite concentrations of 400, 500, 600, 700, 800, and 900 mg/L. There was no significant reduction in sulfate concentration at these bentonite concentrations. Bentonite did not appear to possess any adsorption capacity for sulfate. The results showed that the change in sulfate concentration was marginal during the four-hour study period. Table 3 also shows that during a two-hour study, bentonite leached sulfate into water. Commercial-and laboratory-grade bentonites were used in these experiments. The commercial-grade bentonite leached more sulfate than the laboratory-grade bentonite. Since the commercial-grade bentonite used in the studies would have leached some sulfate into the water, it is likely that any marginal adsorption by bentonite may be offset by this leaching.

Ion Exchange

Figure 2 illustrates the concentration of sulfate and regeneration by ion exchange using spiked tap water with sulfate concentration of

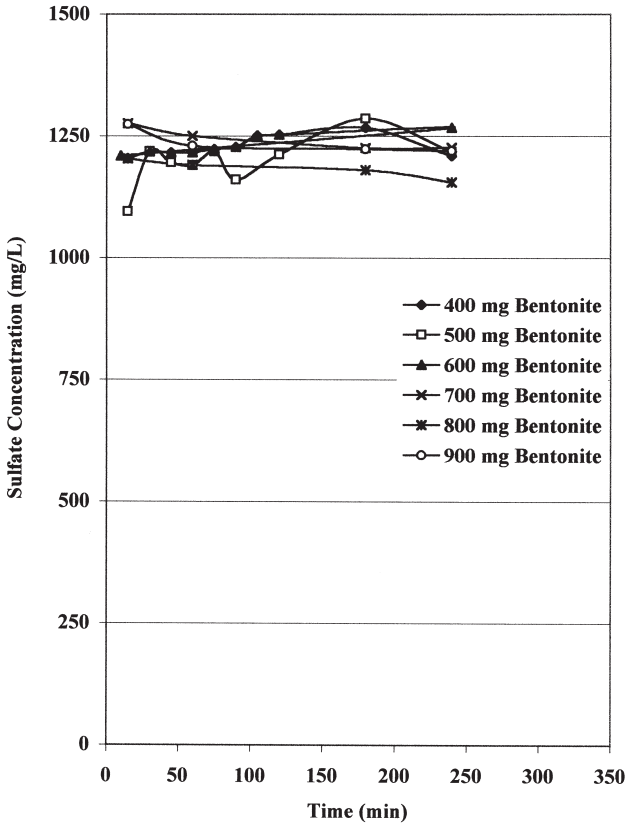

Fig. 1. Average sulfate concentrations in the effluent using different concentrations of bentonite (400, 500, 600, 700, 800, and 900 mg/L) (N = 3).

1000 mg/L. Effluent samples were taken every 30 min until breakthrough occurred. Breakthrough is defined as the concentration of sulfate passing through the column when the absorbent has been saturated with time. The breakthrough of sulfate occurred after 150 min. Sodium chloride at a concentration of 5% was used with tap water to regenerate the column.

Table 3. Sulfate leaching from lab and commercial bentonite

Initial sulfate, mg/L	Commercial bentonite sulfate, mg/L	Laboratory-grade bentonite sulfate, mg/L
25	166	122
25	139	121

Regeneration was complete after 50 min. Within the 50-min regeneration period, the sulfate concentration decreased from 8000 mg/L to <100 mg/L sulfate. Figure 3 illustrates the concentration of sulfate and regeneration using ion exchange with an initial sulfate concentration of 2000 mg/L. Figure 4 compares the sulfate concentration in Leroy and Swift Current samples using the ion exchange system. Initial sulfate concentrations at Leroy and Swift Current were 2280 and 3665 mg/L, respectively. The breakthrough time of sulfate for both samples occurred at approximately 120 min and the removal rates were greater than 90% for both samples. ASB 2 exhibited the capacity to remove sulfate from both waters.

The column removed 21 and 33 g of sulfate from the Leroy and Swift Current water samples, respectively. Regeneration of the column required 180 g of NaCl. The concentration of the regenerant was 40 g/L. Figure 5 shows the regeneration time for Leroy and Swift Current samples. The regeneration cycle required 60 min with an inflow of 75 mL/min.

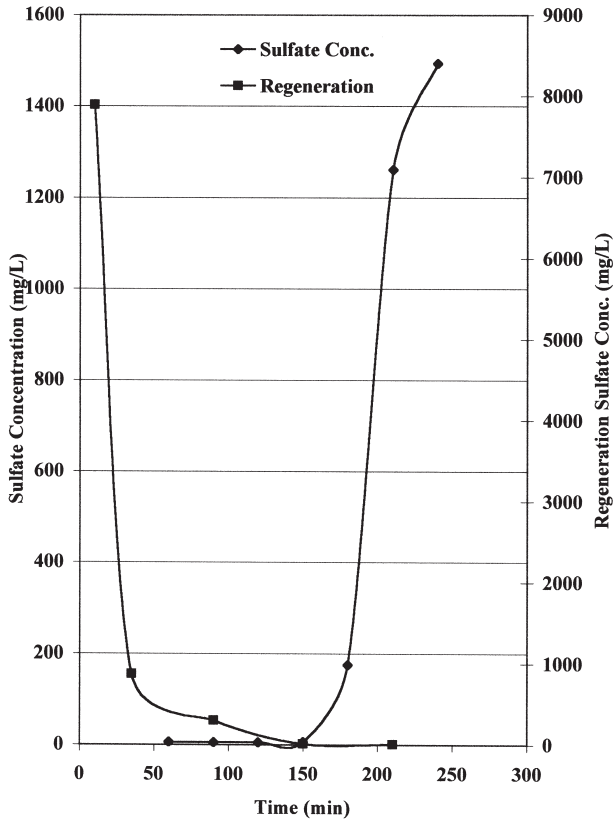

Fig. 2. Average sulfate concentration in the effluent using 1000 mg/L sulfate in tap water (ion exchange and regeneration) (N = 3).

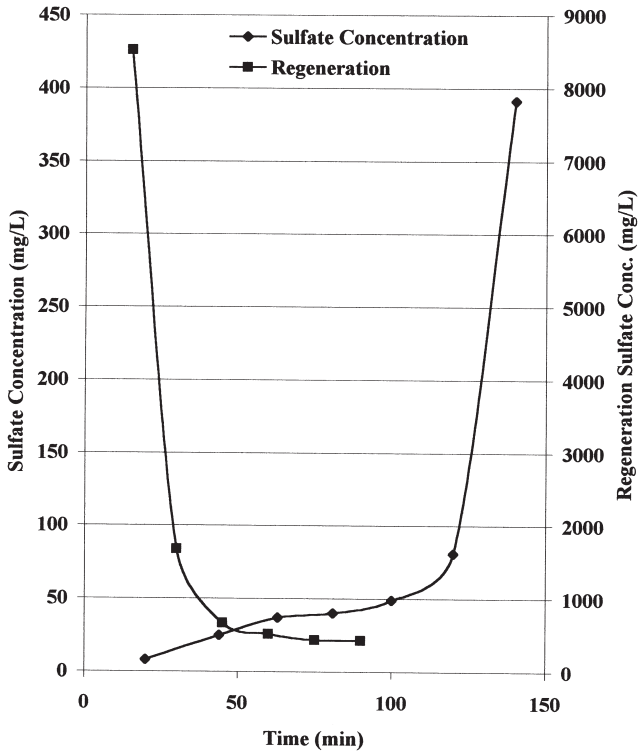

Fig. 3. Average sulfate concentration in the effluent using 2000 mg/L sulfate in tap water (ion exchange and regeneration) (N = 3).

Nanofiltration

Two different pressures of 40 and 80 psi were applied. Low, medium and high sulfate concentrations were used in the runs (see Table 4). It can be seen from the table that the sulfate removal efficiency increased with an increase in applied pressure.

Salt rejection also increased with applied pressure. In both situations, the reduction of sulfate was effective using the nanofiltration system. Under high applied pressure of 80 psi, the removal efficiency was greater when compared to 40 psi. Table 5 shows high sulfate removal for both Leroy and Swift Current samples. It was found that the amount of salt rejection was higher at 80 psi than at 40 psi. The results shown in Table 5 confirm the excellent rejection of sulfate with an average rejection of 93%. Table 6 compares the percentage removal of sulfate by the three technologies. Nanofiltration, while exhibiting slightly higher removal efficiencies, possesses several disadvantages, including lowered removal of sulfates under high TDS in water and membrane fouling from heavy metals such

as iron, and bacteria (American Water Works Association 1990). The most restrictive factor in nanofiltration is scaling by $CaSO_4$. Acidification is required to overcome mineral scaling on membranes (American Water Works Association 1990). Further studies are required to examine the effect of raw water quality parameters on sulfate removal in the context of water supplies studied.

Conclusions and Recommendations

Ion exchange and nanofiltration are the two best available technologies for sulfate removal, and are also proven technologies used for desalination of seawater and brackish water (American Water Works Association 1990). This study showed that ion exchange is the recommended option in removing sulfate from water. Although high amounts of salt are required to regenerate the column, ion exchange appears to be the most beneficial compared to nanofiltration. More detailed studies are

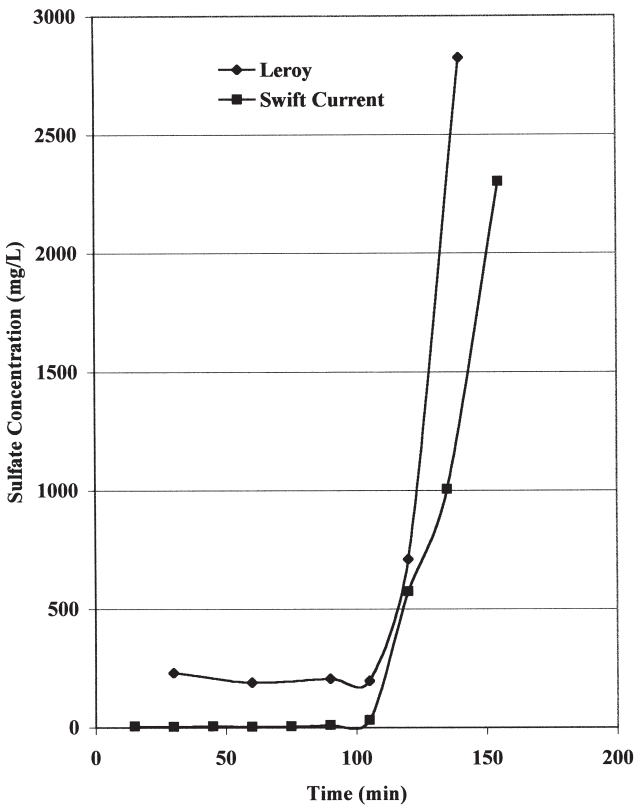

Fig. 4. Average sulfate concentration in the effluent using Leroy and Swift Current samples (ion exchange) (N = 3).

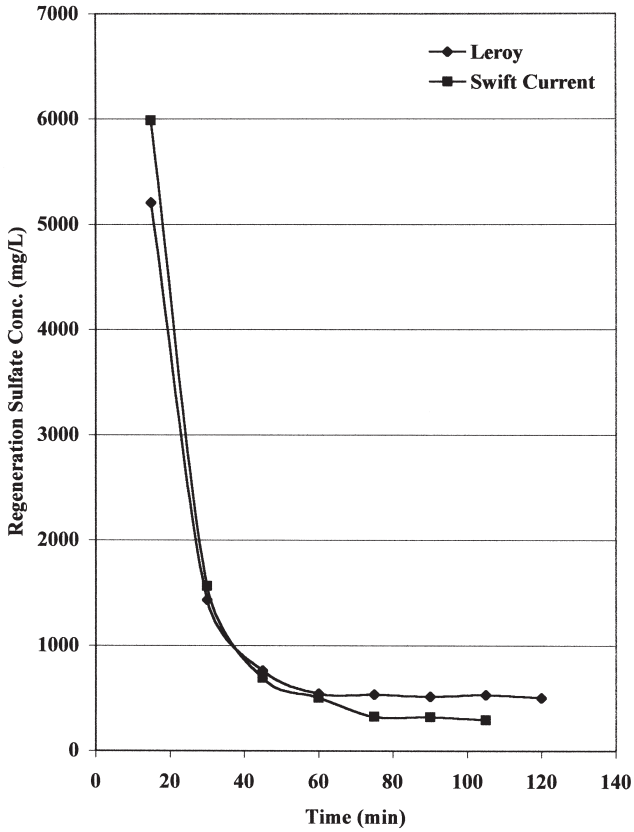

Fig. 5. Regeneration of high capacity, type 2 ionic resin (ASB 2) using sodium chloride.

needed to examine sulfate adsorption by bentonite or kaolinite. In this study sulfate concentration appeared to increase in all the experiments. These results are in contrast to studies by other investigators, who claimed success with bentonite especially when sulfate concentrations were low (less than 50 mg/L).

Table 4. Nanofiltration runs with varying SO_4 concentrations under 40 and 80 psi

Pressure 40 psi			Pressure 80 psi		
Initial Conc. 1650 mg SO_4/L	Prod. Conc. mg SO_4/L	Brine Conc. mg SO_4/L	Initial Conc. 916 mg SO_4/L	Prod. Conc. mg SO_4/L	Brine Conc. mg SO_4/L
Average Conc.	93 ± 4[a]	2172	Average Conc.	67 ± 11[a]	1245
Salt Rejection (%)	94		Salt Rejection (%)	93	
Initial Conc. 2643 mg SO_4/L	Prod. Conc. mg SO_4/L	Brine Conc. mg SO_4/L	Initial Conc. 2810 mg SO_4/L	Prod. Conc. mg SO_4/L	Brine Conc. mg SO_4/L
Average Conc.	199 ± 22[a]	3187	Average Conc.	97 ± 7[a]	3716
Salt Rejection (%)	92		Salt Rejection (%)	97	
Initial Conc. 3600 mg SO_4/L	Prod. Conc. mg SO_4/L	Brine Conc. mg SO_4/L	Initial Conc. 3600 mg SO_4/L	Prod. Conc. mg SO_4/L	Brine Conc. mg SO_4/L
Average Conc.	400 ± 13[a]	4016	Average Conc.	164 ± 21[a]	4597
Salt Rejection (%)	89		Salt Rejection (%)	95	
Initial Conc. 5363 mg SO_4/L	Prod. Conc. mg SO_4/L	Brine Conc. mg SO_4/L	Initial Conc. 4095 mg SO_4/L	Prod. Conc. mg SO_4/L	Brine Conc. mg SO_4/L
Average Conc.	638 ± 23[a]	5883	Average Conc.	144 ± 13[a]	5205
Salt Rejection (%)	88		Salt Rejection (%)	96	

[a]Standard deviation.

Table 5. Nanofiltration runs using Leroy and Swift Current samples under 40 and 80 psi

Leroy					
Pressure 40 psi			Pressure 80 psi		
	Prod. Conc. mg SO_4/L	Brine Conc. mg SO_4/L		Prod. Conc. mg SO_4/L	Brine Conc. mg SO_4/L
Average Conc.	229 ± 1 [a]	3835	Average Conc.	199 ± 31 [a]	2687
Salt Rejection (%)	90		Salt Rejection (%)	91	
Swift Current					
Pressure 40 psi			Pressure 80 psi		
	Prod. Conc. mg SO_4/L	Brine Conc. mg SO_4/L		Prod. Conc. mg SO_4/L	Brine Conc. mg SO_4/L
Average Conc.	296 ± 42 [a]	4251	Average Conc.	127 ± 25 [a]	5132
Salt Rejection (%)	92		Salt Rejection (%)	97	

[a]Standard deviation, initial concentration is 2280 and 3665 mg/L sulfate for Leroy and Swift Current samples, respectively.

Table 6. Percentage removal comparison of the three technologies

	Ion-exchange			Nanofiltration at 80 psi			Bentonite adsorption
Water used	Spiked tap water	Leroy	Swift Current	Spiked tap water	Leroy	Swift Current	Spiked tap water
Sulfate temoval	≅90%	≅90%	≅94%	97%[a] 95%[b]	91%	97%	Nil

[a]At concentration of 2810 mg SO_4^{--}.
[b]At concentration of 3600 mg SO_4^{--}.

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