

# **Arsenic removal from drinking water by flocculation and microfiltration**

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## **Abstract**

Arsenic removal from drinking water is a major problem in many parts of the world. We have investigated arsenic removal by flocculation and microfiltration. Ferric chloride and ferric sulphate have been used as flocculants. The use of small amounts of cationic polymeric flocculants, as flocculation aids in the presence of ferric ions, has also been investigated.

The results obtained here show that flocculation prior to microfiltration leads to significant arsenic removal in the permeate. Further, the addition of small amounts of cationic polymeric flocculants lead to significantly improved permeate fluxes during microfiltration. The residual turbidity, after flocculation and microfiltration, may be used as a guide to the level of arsenic removal. Since energy requirements for microfiltration are low and fluxes high, compared to other membrane processes such as reverse osmosis and nanofiltration, flocculation and microfiltration may be a cost effective method for arsenic removal from drinking water.

*Key words:* arsenic, cationic flocculant, drinking water, ferric ions, flocculation, microfiltration

## **Introduction**

Arsenic occurs naturally in the water in many parts of the world [1]. Arsenic levels of over 60 ppm are lethal for human consumption. In the US the current maximum contaminant level (MCL) in drinking water is 50 ppb [2]. However the United States Environmental Protection Agency (EPA) recently approved new guidelines which will phase in a MCL of 10 ppb [3,4]. The EPA estimates that adopting this lower arsenic standard will require 3,000 community water systems in the US, serving 11 million people, to take corrective action to lower the current level of arsenic in the drinking water [2]. A recent study by the US Geological Survey shows that arsenic concentrations higher than 10 ppb occur throughout the US and that mapping arsenic in groundwater is a very complex problem [5]. There is therefore a great need to develop cost efficient methods for arsenic removal from drinking water.

There are currently many methods for removing arsenic from drinking water [4]. Flocculation using ferric chloride or ferric sulphate followed by sand filtration is commonly employed. In this work we have explored the feasibility of arsenic removal by flocculation and microfiltration.

## Experimental

Water samples were obtained from the City in southern Colorado. Table 1 gives a typical average water analysis. The average arsenic concentration in the drinking water was 42 ppb. These water samples were treated with either ferric chloride or ferric sulphate in a six paddle jar tester (Phipps and Bird, Richmond, VA, USA). In addition, small amounts of cationic polymeric flocculants obtained from Cytec Industries (Stamford, CT), were added to some of the samples prior to microfiltration. The pH of the water was adjusted using NaOH, HCl or H<sub>2</sub>SO<sub>4</sub>. Microfiltration was conducted using mixed esters of cellulose acetate and cellulose nitrate membranes with pore sizes of 0.22 and 1.2 µm.

Table 1 Average water analysis for drinking water

Analyte	Concentration (mg/L)	Analyte	Concentration (mg/L)	Analyte	Concentration (mg/L)
PH	8.3	Turbidity (NTU)	0.37	TSS	0.2
Alkalinity Total (as CaCO <sub>3</sub> )	92.5	Nitrate (as N)	0.1	Nitrite (as N)	<0.05
Calcium	6.5	Magnesium	0.21	Potassium	6.6
Chloride	0.77	Fluoride	1.07	Sodium	52.9
Silica	141.1	Sulfate	9.2	Aluminum	<0.02
Chromium	<0.006	Iron	0.035	Arsenic	0.042
Manganese	0.003	Orthophosphate as P	0.180		

## Results

Figure 1 shows the variation of arsenic concentration with residual water turbidity. For the water samples tested here, an almost linear relationship is obtained. Table 2 gives the final arsenic concentration and turbidity in the filtrate after microfiltration. In addition, some of the flocculated samples were allowed to settle and the arsenic concentration and turbidity of the supernatant determined. These results are also given in Table 2. As can be seen, microfiltration leads to more rapid and complete arsenic and turbidity removal than sedimentation.

Figures 2-5 summarize the microfiltration results. In these figures the percent arsenic removed is plotted against the ferric ion concentration. As can be seen the pH of the water has a strong effect on the percent arsenic removed at a given ferric ion dose. Further, it is the total ferric ion present that is important in determining the level of arsenic removal. The ferric chloride and ferric sulfate dose required to remove a given percentage of arsenic is the same if compared on the basis of total ferric ion present.

Comparing Figures 2 and 3 with 4 and 5 it can be seen that for a given ferric ion

dose, membranes with a nominal pore size of 0.22  $\mu\text{m}$  remove more arsenic than membranes with a nominal pore size of 1.2  $\mu\text{m}$ . The effectiveness of a given membrane pore size depends on the floc size distribution. The particle size distribution was measured using a Coulter (Miami, FL, USA) LS 230 laser diffraction particle size analyzer. Figure 6 gives a typical floc size distribution.

The effect of adding cationic polymeric flocculants as filter aids is shown in Figure 7. The raw water with adjusted pH 6.8 was flocculated with 10 ppm  $\text{FeCl}_3$  and filtered using a 0.2  $\mu\text{m}$  pore size membrane. In the absence of polymer the permeate flux drops to about 50% of the water flux (permeate flux of the clean membrane in the absence of particulate matter) in less than 1 hour. However upon the addition of 0.3 ppm 2461 (cationic polyacrylamide, MW  $10^7$ , Cytec Industries) the permeate flux remains constant at the water flux for over 3 hours.

## Discussion

Arsenic adsorption by iron complexes occurs by ligand exchange of the As species for  $\text{OH}_2$  and  $\text{OH}^-$  in the coordination spheres of surface structural Fe atoms [6]. Arsenic removal by microfiltration depends on entrapment of the floc particles by the membrane. The turbidity of the raw water after flocculation depends on the number of floc particles present. It is not surprising therefore that the lower the permeate turbidity the lower the final arsenic concentration in the permeate. Use of permeate turbidity as an indicator of the residual arsenic concentration is qualitative measure which may be used to determine appropriate flocculation conditions. However the actual amount of arsenic that adsorbs onto iron complexes depends on many factors.

Arsenic exists in two main oxidation states, arsenite, As(III) and arsenate, As(V). The predominate oxidation state depends on the pH and the redox potential. Both forms have strong affinities for iron complexes however they behave oppositely with respect to pH. In general in the pH range 3-10, adsorption of arsenate decreases with increasing pH while the adsorption of arsenite increases [7]. Figures 3-6 show that the level of arsenic removal in the filtrate after flocculation and microfiltration is pH dependent as expected.

In this study, the ferric ion dose required, was the same for ferric chloride and ferric sulfate. Thus the presence of sulfate ions had little effect on arsenic removal by the iron compounds. While Jain and Loeppert [7] observed a similar result, others [8] have reported a considerable decrease in arsenic adsorption in the presence of sulfate ions. These results highlight the fact that the effect of sulfate ions depends not only on the arsenic concentration but also the concentration of other electrolytes present. The amount of arsenic adsorbed onto the ferric complexes present and therefore the ferric ion dose required depends on the concentration of other dissolved species present.

Removal of arsenic by flocculation and microfiltration depends on the effectiveness of arsenic adsorption onto the ferric complexes present and on the rejection of the arsenic containing flocs formed by the membrane. The larger the membrane pore size, the lower the resistance to filtrate flow and hence the lower the pumping costs for a given filtrate flow rate. However the larger the pore size the larger the number of smaller flocs that are able to pass through the membrane into the filtrate. The results obtained (see Figures 2-5) suggest that for a given ferric ion dose and pH, 0.22  $\mu\text{m}$  membranes are more successful in removing arsenic

than 1.2  $\mu\text{m}$  pore size membranes.

The particle size distribution may be used to guide the selection of an appropriate membrane pore size. Figure 6 shows that for the experiments conducted here, a number of submicron sized particles exist which would pass through 1.2  $\mu\text{m}$  pore size membranes more easily than 0.22  $\mu\text{m}$  pore size membranes. The optimum practical membrane pore size however will depend not only on the particle size distribution but also on the pumping costs.

Table 2 shows that flocculation followed by microfiltration is significantly better than flocculation followed by sedimentation for arsenic removal. In addition tangential flow microfiltration has a number of advantages. Since the membrane pores are large, 0.22  $\mu\text{m}$  or larger, the pumping costs are much lower and fluxes much higher than other membrane based separation processes such as nanofiltration and reverse osmosis [9]. Further microfiltration modules are easy to scale up and membrane cleaning is simple. The results obtained here suggest that flocculation and microfiltration may be a cost effective method for arsenic removal from drinking water.

The use of cationic polymeric flocculants as flocculation aids has been described by previous investigators [10-11]. Figure 7 shows that the addition of a small amount of cationic polymeric flocculant can lead to significant improvements in fluxes. Not only is the permeate flux higher, addition of a small amount of polymeric flocculant is also likely to increase the run time before the membrane cleaning is necessary. Polymeric flocculants are however more expensive than ferric chloride or ferric sulphate. Thus the economic viability of adding small amounts of cationic flocculants depends on the quality of the raw water.

### Conclusion

The feasibility of flocculation and microfiltration for arsenic removal from drinking water has been investigated. Flocculation using ferric ions can lead to significant arsenic adsorption onto the ferric complexes present. However the efficiency of this adsorption depends on the pH of the water and the presence of other ions. Microfiltration of the flocculated water results in rejection of the flocs formed by the membrane thus leading to low turbidity and arsenic removal in the filtrate. Addition of small amounts of cationic polymeric flocculant can greatly increase the permeate flux during microfiltration.

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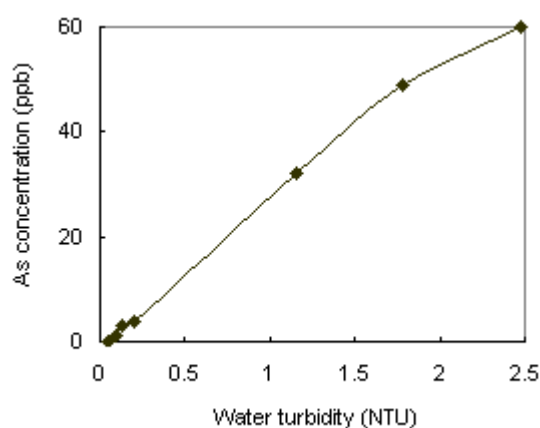


Figure 1 Variation of arsenic concentration with turbidity

Table 2 Comparison of arsenic removal by flocculation and microfiltration, and flocculation and sedimentation. The raw water was treated with 7.5 mg/L Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (based on

ferric ion). The pH of the water was 6.8 and the initial arsenic concentration was 60 ppb.

Time (min)		0	20	60
Sedimentation	As conc. (ppb)	60	49	32
	Turbidity (NTU)	2.48	1.78	1.16
Microfiltration	As conc. (ppb)	1	1	1
	Turbidity (NTU)	0.09	0.09	0.08

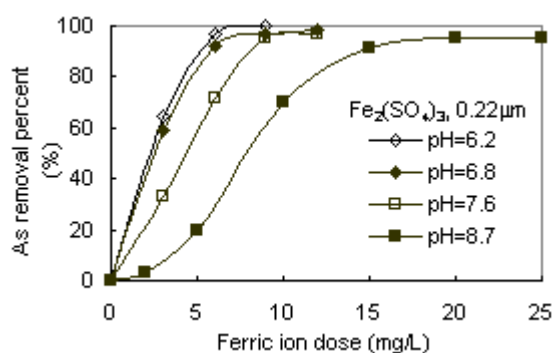


Figure 2 Variation of percent arsenic removed with ferric ion dose, added as ferric sulfate. After flocculation the feed was filtered using a 0.22 µm pore size membrane.

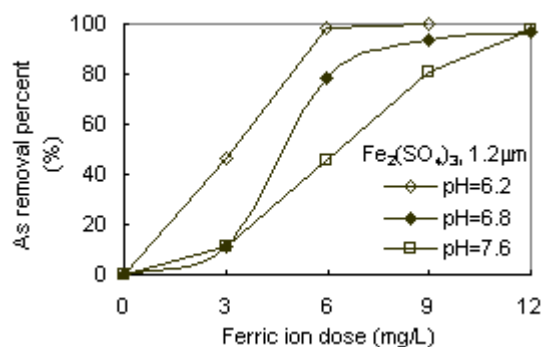


Figure 3 Variation of percent arsenic removed with ferric ion dose, added as ferric sulfate. After flocculation the feed was filtered using a 1.2 µm pore size membrane.

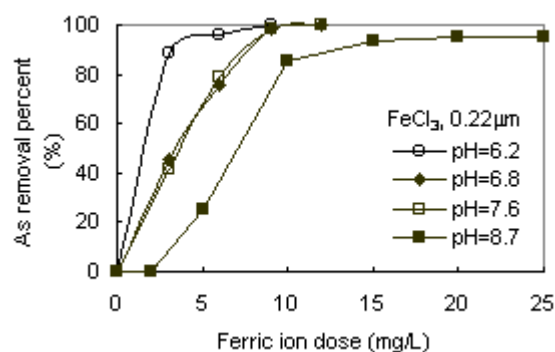


Figure 4 Variation of percent arsenic removed with ferric ion dose, added as ferric chloride. After flocculation the feed was filtered using a 0.22  $\mu\text{m}$  pore size membrane.

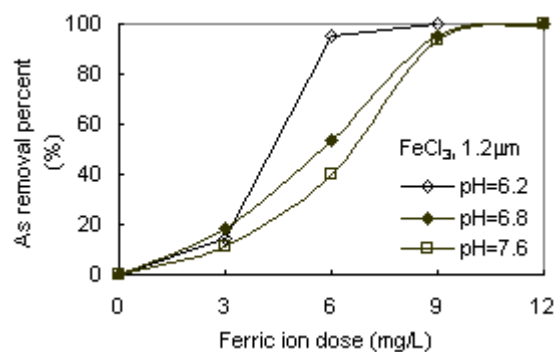


Figure 5 Variation of percent arsenic removed with ferric ion dose, added as ferric chloride. After flocculation the feed was filtered using a 1.2  $\mu\text{m}$  pore size membrane.

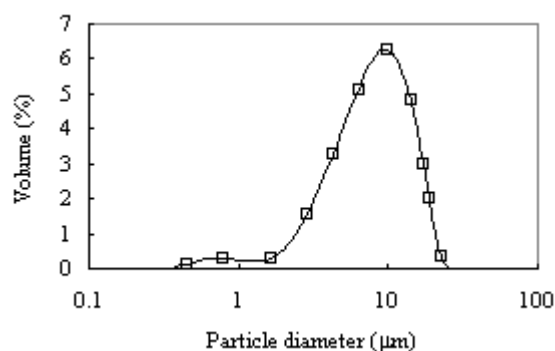


Figure 6 Typical particle size distribution after flocculation with ferric chloride. The percentage by volume of a given particle size is plotted against the particle size in  $\mu\text{m}$ .

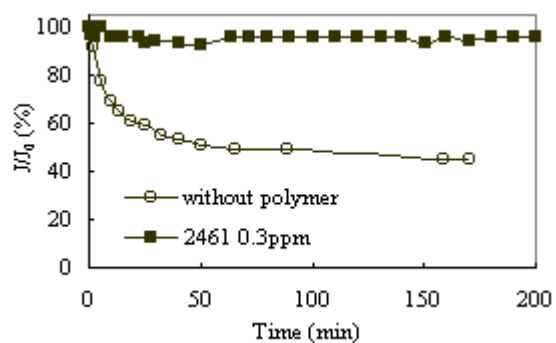


Figure 7 Comparison of microfiltration performance with and without addition of polymer

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