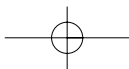


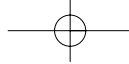
ORGANIC FOULING OF ANION ION EXCHANGE RESINS

Reducing the Risk of Occurrence

PUR**LITE**

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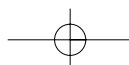
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INTRODUCTION

This bulletin deals with the efficient removal of organic matters and colloids from water.

Ion Exchange resins, generally speaking, remove organic matter from water particularly well, but unless care is taken in the selection of the ion exchanger plus in certain cases the correct pretreatment process, then rapid fouling of the ion exchange resin can occur and this fouling is often irreversible.

THE COMPOSITION OF ORGANIC MATTER FOUND IN WATER

The various species of organic matter can be subdivided into two main groups

(a) Insoluble

- eg. Various particulates of vegetable or animal origin
- Certain humic matter
- Micro-organisms
- Vegetable and mineral oils

(b) Soluble

- eg. Humic and fulvic species
- "Industrial" synthetic organics
- Saccharides
- Certain amino acids and proteins

The insoluble matter is usually removed by coagulation and filtration techniques leaving the soluble and colloidal species in the supernatant water.

The key soluble species that have to be considered in most surface derived waters are humates and fulvates.

Many researchers have endeavoured to define the molecular structure of these compounds and it is still uncertain whether they are present in raw waters as acids or as salts.

A simplified structure for humic acid has been proposed by certain workers (Fig. 1)

However, more recent evidence suggests a more complicated structure that can have heavy metals complexed with the groups attached to the aromatic structure (Fig 2)

It can be appreciated from both Fig 1 and especially from Fig 2 that this complex molecule when absorbed onto an anion resin will not only cause potential organic fouling but also is likely to deposit heavy metals within the resin matrix which cannot be removed by caustic soda regeneration.

The fulvic acid type structure has not been so well defined as the humic acid but it is thought to be smaller in size and present in water in similar concentrations.

In the case of water containing colloidal matter which persists after coagulation - filtration, the colloidal particles can often occur as complex mixtures of organics - silica - heavy metals. Normally, because the organics and heavy metals are bound together by colloidal silica, they are not removed by normal ion exchange resin and pass forward into the final treated water. When this water is used for boiler feed, it is not always realised that these complex colloidal particles are contributing silica, organics and heavy metals to the boiler water analysis and boiler operators can often misinterpret the presence of these species as being caused through malfunctioning of the ion exchange demineralisation plant.

If this problem persists, either more efficient coagulation has to be carried out (possibly using ferric chloride) prior to the water being fed to the ion exchange plant, or ultrafiltration can be considered.

In instances of lower flow ultra pure water plants, Purolite A 501P can remove colloidal particles to extremely low levels and this category of resin is used particularly in the electronics industry when the water specification calls for nil particulates and 18 megohm resistance quality.

Fig. 1

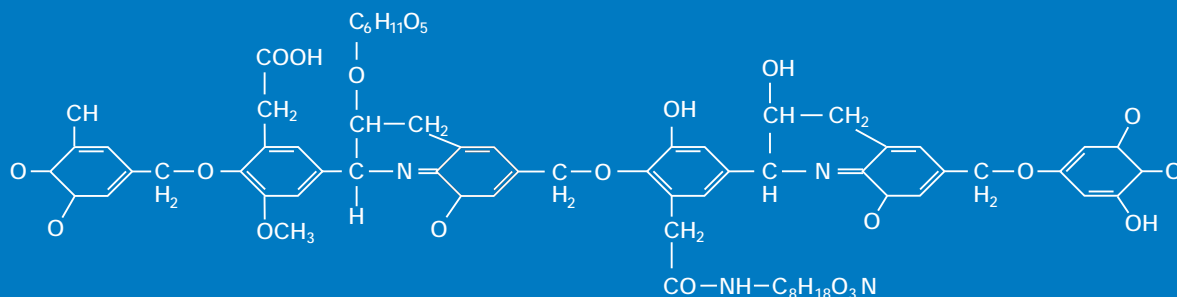
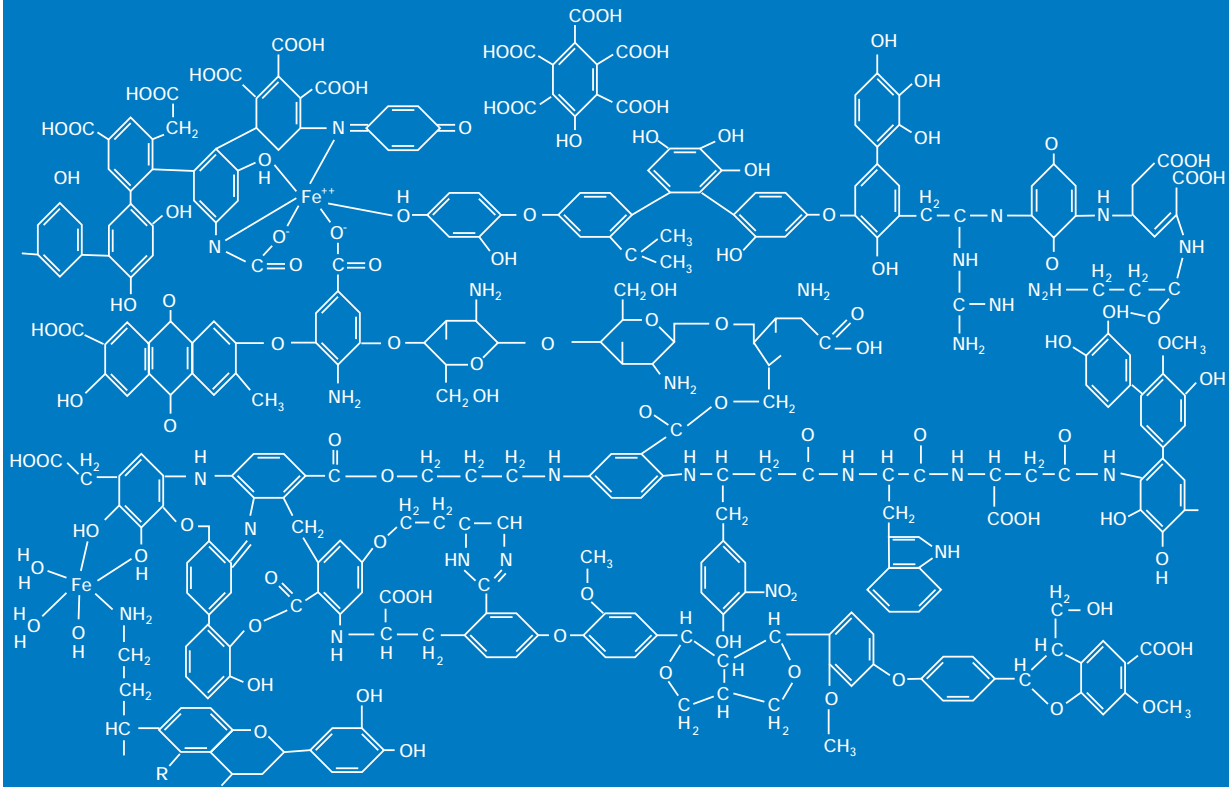


Fig. 2



THE MEASUREMENT OF ORGANICS IN WATER

There are two key methods used routinely at the present time; Total Organic Carbon (TOC) measurement by instrument or the employment of potassium permanganate solution to oxidise the organics and then to back titrate the excess potassium permanganate with sodium thiosulphate. Purolite recommend the T.O.C. method conforming with ASTM D4779-93.

The comparison between the organics concentration stated in a water analysis depends upon the various analytical techniques. Table I shows the relationship between the figures recorded against the different analytical methods.

The T.O.C. figure resulting from the ASTM D4779-93 test result in a lower number compared to results obtained by either the U.V. method or one of the various potassium permanganate procedures.

Table I

For a given water the table shows the comparison of results version T.O.C. as 1ppm Carbon.

Method	Concentration
T.O.C.	1 ppm
KMnO ₄ - 10 min boil (Kubel)	3 ppm as O ₂ 12 ppm as KMnO ₄
KMnO ₄ - 30 min at 100°C	2 - 2.5 ppm as O ₂ 8 - 10 ppm as KMnO ₄
KMnO ₄ - 4 h at 27°C	1 ppm as O ₂ 4 ppm as KMnO ₄
Ultra Violet	3 ppm

THE MECHANISM OF ORGANIC FOULING

Within the context of this paper, only organic fouling of anion exchange resins is dealt with although proteins polyelectrolytes, detergents and certain saccharides can foul cation resin.

The retention of soluble organics such as humic and fulvic acids from water by anion exchange resin involves two mechanisms - ionic exchange and physical (Van der Waal's) forces.

During the progressive exhaustion of an anion resin in a normal demineralisation process the resin will not only exchange inorganic ions (chloride, sulphates etc) but also exchange/adsorb organics.

The large complex organic molecules as depicted in Figs 1 and 2 diffuse slowly into the anion resin and are held within the resin matrix by the mechanisms outlined above. The diffusion of organics out of the resin during normal regeneration with caustic soda is also slow but has to occur during the relatively short regeneration cycle. The tendency therefore in instances when organics are present in the water, is for the anion resin to progressively retain a little more organic matter each cycle than is being eluted during regeneration. Thus the resin steadily becomes "irreversibly" fouled as far as normal operation is concerned.

THE FOULING POTENTIAL OF WATERS

The fouling potential of a water is not solely related to the level of organics per se.

The most important feature of the water analysis is the ratio of organics to total inorganic anions expressed as CaCO_3 . Purolite

recommends that the following equation is used in order to provide an "N" factor.

$$N = \frac{\text{mg/l of T.O.C.} \times 900}{\text{mg/l of total inorganic anions as CaCO}_3}$$

The following table illustrates a guide to correlation between the "N" factor and the choice of weak or strong base anion resin (or system)

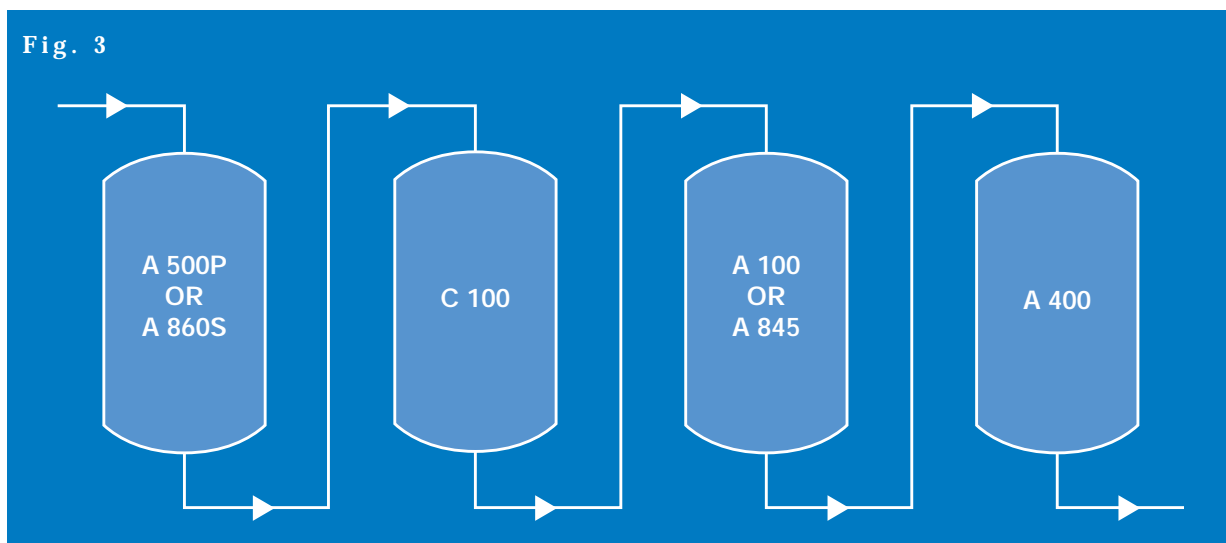
Table II

"N" Factor	Choice of Resin
< 1	Purolite A400/A200 Type I or II gel polystyrene
1 - 2	Purolite A500 Type I macroporous styrene
2 - 3	Purolite A510 Type II macroporous styrene
3 - 4	Purolite A850/A870 Type I acrylic or (dual base)
4 - 6	Purolite A100 tertiary amine weak base polystyrene
6 - 8	Purolite A845 tertiary amine weak base acrylic (or A847)
> 8	Purolite A500P Organic scavengers or A860 (used as a pre-treat column to protect the working anion units)

Table II refers to the "N" factor of the water actually coming into contact with any single resin.

For example, in a demineralisation system you may have the sequence of units shown in Figure 3.

Thus the main proportion of organics is taken out on the organic scavenger resin - Purolite A500P or A860S and a further proportion removed by the Purolite A100 or A845 before the water passes through the Purolite A400. Also the "N" factor can alter after degas (removal of carbon dioxide).



THE EFFECT OF FOULING ON THE PERFORMANCE OF ION EXCHANGE RESIN

Earlier in this bulletin the types of molecular structure associated with organics are illustrated and it can be seen from Figures 1 and 2 that these organic molecules have high molecular weights and are much larger than common inorganic ions (chloride, sulphate, nitrate etc.), and therefore tend to block and interfere with the normal ion exchange properties of the resin.

If organics are allowed to accumulate on a resin the following effects can be observed:-

- **Reduction in water quality**
- **Lower operating capacity**
- **Higher rinse requirements**

If the exchange sites on an anion resin are partially screened by large organic molecules the speed of exchange of inorganic ions from the water onto the resin will be slower. In the case of a strong base resin where silica removal is important, because the silica ion is only weakly dissociated in solution, organic fouling of the resin can cause an increase in silica leakage.

In addition, sodium ions originating from the sodium hydroxide regeneration step, substitute onto the carboxylic groups contained within the organic foulant molecule. This substitution of sodium creates the long rinse problem associated with organically fouled anion resins by causing slow hydrolysis of the sodium off the resin.

Due to the combined effects described above, the operating capacity is reduced because of the constraints on what constitutes "acceptable water quality".

CHOOSING THE RIGHT RESIN SYSTEM

As with any design of ion exchange system, the influent water analysis and the required treated water quality have to be fully defined.

Under the section on fouling potential of water, a method of choosing the correct anion resin against the water analysis is described.

If we take the ion exchange resin sequence illustrated on page 4, as an example, we can assume that the raw feed water has an "N" factor higher than 8 and hence the inclusion of our organic scavenger unit is considered.

Taking a specific example of a raw water with an "N" factor of 18; by passing the water first of all through Purolite A 500P the "N" factor can be reduced to 5 - 6. Because of the "N" factor still being rather high, a weak base resin such as Purolite A 100 or A 845 should be considered. Use of one of these resins would reduce the "N" factor to < 1 and so a normal Type I resin such as Purolite A 400 can then be employed without the risk of organic fouling.

ORGANIC SCAVENGERS

When the "N" factor is above 8, the use of Purolite A500P or A860S (organic scavengers) is recommended.

These scavengers operate alone or in chloride form and are regenerated with 10% sodium chloride with 2% sodium hydroxide. They are designed on a flow rate basis (circa 15 - 20 BV's/h depending upon the organic concentration in the water).

A working capacity for organic removal on Purolite A 500P is 3g/l as carbon and a similar capacity can be achieved on Purolite A 860S. The actual capacity can be much higher but it is recommended that organic scavengers are underworked so as to maintain their efficiency over a long period.

Far more efficient elution of organics can be achieved when the regenerant is applied at temperatures between 40° - 50°C.

RESIN MAINTENANCE AND CONCLUSIONS

- **Prevention of organic fouling is better than cure.**
- **Laboratory and plant trials have shown that where total removal of organics is required the use of styrene and acrylic resin in sequence is recommended.**
- **Acrylic resins are superior to the equivalent styrenic types on resistance to organic fouling. There are two reasons for this, firstly the acrylic matrix is more hydrophilic and secondly the aliphatic acrylic structure is more accessible and allows an easier exit path for the organic molecules.**

There are certain basic rules that should be followed.

1. **Choose the correct resins by using the "N" factor table.**
2. **Do not allow the resin beds to overrun.**
3. **Use a relatively high regeneration level to ensure efficient removal of organics.**
4. **With regard to (2) use the capacity data in the "Puredesign" computer programme which allows adjustments of the actual operating capacity in line with the level of organics in the feed water.**

APPENDIX - CLEAN UP PROCEDURE FOR ORGANICALLY FOULED RESINS

It is well known that anion resins are susceptible to fouling by the humic and fulvic acids often found in surface waters.

These organics species, because of the relatively large molecular weights, become trapped within resin matrix (to a greater or lesser degree depending upon the resin) and specific procedures have to be employed to recover the original ion exchange properties of the resin.

The symptoms of organic fouling include long rinse requirements, poor capacity and, in the case of strong base resin, higher silica leakage.

Treatment

The most common forms of treatment involve the use of caustic brine solution, the procedure is as follows:-

- **The resin should be treated at the end of the normal exhaustion cycle.**
- **Three bed volumes of 10% w/v brine solution containing 2% w/v caustic soda should be prepared.**
- **One bed volume should be introduced into the ion exchange units at a flow rate not exceeding 2 BV's per hour followed by a second bed volume - this second bed volume should be retained in the unit for as long as possible but at least 2 hours. Some agitation, if possible, should be employed periodically throughout the retention period.**
- **At the end of the retention period the last bed volume of brine should be passed through the resin at a rate of 1 BV per hour and the resin thoroughly rinsed with clean water until free from brine.**
- **The resin should be subject to at least two complete regenerating cycles before being put back on line.**

N.B. Brine at minimum 35°C should be employed or preferably as high as 60°C so as to produce a better organic elution effect.

IRON/ORGANIC COMPLEXES

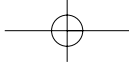
This subject is covered to some extent in the Purolite bulletin on Iron Fouling.

Occasionally the presence of iron is detected on the anion resin. This can arise from an iron/organic complex being present in the raw feed water.

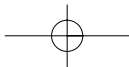
In these cases, it is advisable to consider treatment of the anion resin with 6% hydrochloric acid first, before the brine treatment. The procedure that should be followed is similar to that given for brining.

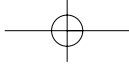
It is extremely important that all traces of hydrochloric acid are removed from the unit before introduction of caustic brine.

It is also important to ensure that the materials of construction are suitably resistant to hydrochloric acid.

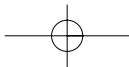


Notes





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