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CHAPTER 5 TREATMENT OPTIONS (LEVEL 1)

If toxic blooms occur despite management strategies, there are three options to minimise toxin levels in water supplied to consumers;

- Use of an alternative supply uncontaminated by cyanobacterial toxins
- Offtake manipulation to prevent the intake of cyanobacteria and/or their toxins into the water supply system
- Water treatment to remove cyanobacterial cells and/or their toxins

The main focus of this section is the removal of cyanobacterial cells and the cyanotoxins they produce. However, for many treatment plants a first control step can be the manipulation of the offtake from the source water to minimise cyanobacteria entering the treatment facility.

OFF-TAKE MANIPULATION

Due to the buoyancy regulation of some cyanobacteria, they are usually found in a particular depth range within a water body. A comprehensive monitoring program, as described in Chapter 3, will provide this information. If the treatment plant has the ability to extract water from several depths, often the most concentrated area of the cyanobacteria bloom can be avoided. However, the conditions that favour the growth of cyanobacteria (thermal stratification, anoxic hypolimnion) will also favour release of iron and manganese from the sediments, so care should be taken to adjust the height of the offtake to avoid both high cyanobacterial numbers, and elevated manganese and iron levels. Often the two water quality goals will be difficult to manage simultaneously.

CYANOBACTERIAL CELL REMOVAL

A healthy cyanobacterial cell can have high levels of toxin – or taste and odour compounds – confined within its walls. For example, for *Microcystis aeruginosa* more than 95% of the toxin can be contained within healthy cells, whereas the number would be around 50% or less for *Cylindrospermopsis raciborskii*. Therefore, high cell numbers can result in high total toxin concentration. The most effective way to deal with high total toxin concentrations is to remove the cells, intact and without damage. Any damage may lead to toxin leakage, and an increase in the dissolved toxin concentration entering the treatment plant. Dissolved toxin is not removed by conventional treatment technologies, and the aim should be to minimise the levels entering the treatment plant.

Removal of intact cells and associated intracellular toxin should be the primary aim in the treatment of cyanobacteria. As most water treatment processes are designed to remove particulate material as the primary focus, this first step requires only the optimisation of existing particulate removal processes, as well as an awareness of how some of these processes may lead to cell damage, and leaking of the toxins into the dissolved state.

PRE-OXIDATION

Pre-oxidation is not recommended in the presence of potentially-toxic cyanobacteria. Chemical oxidation can have a range of effects on cyanobacteria cells, from minor damage to cell walls to cell death and lysis [1]. Although it has been reported in the literature that oxidation at the inlet of the treatment plant can improve the coagulation of algal cells through a number of mechanisms, [2] the risk of damaging the cells and releasing toxin into the dissolved state is high. If pre-oxidation must be applied in the presence of cyanobacterial cells the levels of oxidant should be sufficient to meet the demand of the water including cells, and result in a residual sufficient for destruction of dissolved toxins if

these are susceptible to removal by the particular oxidant (see following sections on removal of dissolved toxins). If insufficient oxidant is applied there is a risk of high levels of dissolved toxin and organic carbon entering the treatment plant and adversely influencing subsequent removal processes. However, this effect will depend on the oxidant and its reactivity with the particular cyanobacteria. For example, recent work by Ho et al. [3] has shown that potassium permanganate, applied at a concentration necessary to oxidise moderate levels of managanese, did not damage *Anabaena circinalis* cells, and therefore did not result in release of geosmin and saxitoxins into the dissolved state. If pre-oxidation is deemed necessary, it is recommended that laboratory tests be carried out to determine the effect, if any, on the cyanobacteria present in the inlet to the plant.

MICROSTRAINING

Microstraining is a technique that can be used to remove fine particles including algae and cyanobacteria. Microstrainers separate solids from raw water by passage through a fabric of either fine steel mesh or plastic cloth. Depending on the size of aperture in the fabric, it behaves either as a filter to remove coarse turbidity, zooplankton, algae, etc. or as a fine screen to remove larger particles. A microstrainer consists of a horizontally mounted, slowly rotating drum with sides of fabric. One end is sealed and the other allows water in and screenings out. Water is fed into the centre and flows out through the sides. The top of the drum remains above the water level and is continuously cleaned by water jets on the outside. The screenings are collected in a trough suspended towards the top of the drum interior. They are sieved, the solids disposed of and the water returned to the inlet.

Microstraining is used to remove mineral and biological solids from surface water. It is normally used as pre-treatment before slow sand filtration or coagulation processes, but for very good quality waters it can be used as a sole treatment prior to disinfection. Microstraining can successfully remove filamentous or multicellular algae, but will be less efficient for small, unicellular species.

For more details follow this link.

RIVERBANK, SLOW SAND AND BIOLOGICAL FILTRATION

Riverbank filtration is a simple and effective treatment process which is widely used in some parts of the world. Water is abstracted from rivers by using bores (wells) close by, effectively filtering the raw water through the riverbank, usually consisting of sand, gravel or stones. Particulates including algae and cyanobacteria are removed by this filtration process. Many soluble contaminants are also removed by adsorption or by biological processes taking place in the biofilm on the sand/gravel grain surfaces, mainly in the first few centimetres of infiltration. In this process dissolved toxins can also be removed [4]. Bank filtration covers a wide range of conditions, with travel times between the river and the well of a few hours to several months. In case of short travel times the processes involved are comparable to those occurring in slow sand filters.

GENERAL CONSIDERATIONS

Slow sand filtration (SSF) is capable of providing a high degree of removal of algal cells (>99%) and associated cyanotoxin. Biological activity within slow sand filters may also provide some removal of extracellular toxin. Algal growth in the water above slow sand filters is a common problem, and has implications in relation to cyanotoxins, depending on the predominant algal species.

In general, good performance of slow sand filtration depends on the following factors:

1) Feed water quality
   The quality of water going on to slow sand filters is crucial to performance. Generally, turbidity above 10 NTU can lead to reduced run times. In addition, high algal concentrations in the raw water can result in excessive algal growth above the sand, causing rapid blockage and short run lengths. These problems can be alleviated or prevented by pre-treatment (e.g. roughing filters, microstrainers), or by covering of the filters where this is practical.
2) Filtration rate
   Headloss across the bed and the rate of headloss build-up (filter blockage) both increase with increasing filtration rate. Performance of slow sand filtration is best when the filtration rate is constant, avoiding sudden large changes in filtration rate (± 20%) to prevent deterioration in filtrate quality.
3) Sand skimming
   Groups of filters should be skimmed in rotation, such that at any time a minimum number of filters are out of operation, thereby preventing excessive loading to the other filters. Skimming involves removing the schmutzdecke layer and the uppermost 1 to 2 centimeters of sand, manually or, more commonly now, using mechanical scrapers. The bed depth should not be allowed to decrease to less than 0.3 m; the depth is then returned to between 1 and 1.5 m using cleaned sand from storage.
4) Restart after sand skimming
   A ripening period of several days is required before good performance is restored after skimming. Longer periods may be necessary after resanding or at low water temperatures. To prevent excessive penetration of solids into newly skimmed or resanded beds, the filtration rate should be gradually increased over a period of 3 or 4 days, starting at a low rate of less than 0.1 m/hour. The filtrate produced during the first few days after restart may need to be discharged to waste or returned to the inlet of the other filters

Specific information relating to removal of cyanotoxins by slow sand filtration is scarce, partly because laboratory scale tests are not appropriate since they cannot easily simulate the biologically active schmutzdecke layer.

Bank filtration covers a wide range of settings with travel times between the river and the well of just a few hours to several months. In case of short travel times the removal is similar to that described for SSF, though a schmutzdecke is usually not formed along the river bank due to shear stress of the flowing river water. Regular skimming is therefore not necessary. In this setting most intra-cellular toxins will be removed from the source water. In case of longer travel times (several days to months) additional degradation of extra-cellular toxin is possible. Mixing with ambient landside groundwater in the drinking water well will result in further reduction of concentrations.

For more details, follow this link.

CONVENTIONAL TREATMENT

The response of cyanobacteria to coagulants and other chemicals used during the coagulation/flocculation process depends strongly on the type of organism and its form (i.e. individual cells, filamentous etc, see *Chapter 1*). As a result, specific guidelines for coagulation are not possible. However, general tips for optimum removal of cyanobacteria will be helpful as a first treatment step.

If optimisation of coagulation is maintained for the normal parameters (turbidity, dissolved organic carbon removal etc) under the conditions of high numbers of cyanobacteria, optimum removal of cells, and therefore intracellular toxin, will be achieved [5]. Evidence in the literature is conflicting regarding the most effective coagulant, polyelectrolytes, etc, so optimising the existing processes should be the first response. Evidence is also conflicting in terms of damage to the cells during the coagulation process. Whether there is some damage during the process appears to be dependent on the health of the cells, and the stage in the growth of the bloom. In a natural bloom there will probably be cells in all stages of growth. However, an optimised coagulation process will provide a very effective first barrier to toxic algae in the

treatment plant. Figure 5-1 shows an *Anabaena Circinalis* filament encased in an alum floc. The darker areas are the powdered activated carbon particles used to remove dissolved toxins and taste and odour compounds.

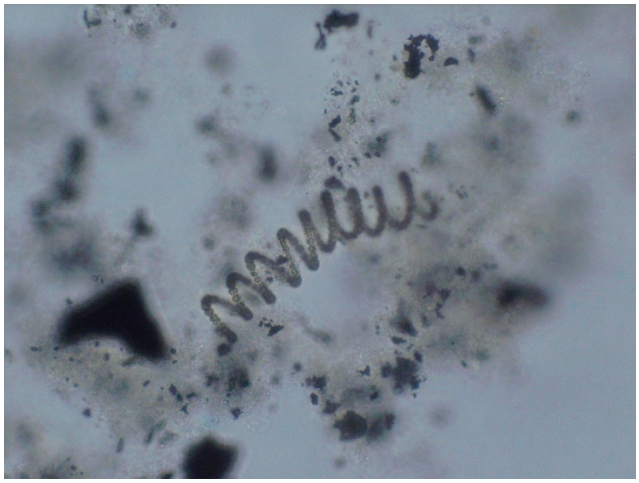

Figure 5-1 *Anabaena* filament encased in an alum floc. Dark areas are powdered activated carbon particles used to remove dissolved tastes and odours and cyanotoxins.

Dissolved air flotation (DAF) is very effective for the removal of cyanobacterial cells, particularly for those species with gas vacuoles that may render them more difficult to settle. The same advice for the optimisation of the process applies for the DAF process.

COAGULATION AND FLOCCULATION GENERAL CONSIDERATIONS

Optimisation of the coagulation process is important under all conditions, but it is particularly relevant during a toxic cyanobacteria bloom. Achieving good chemical coagulation and flocculation relies on the following:

- Selection of most appropriate coagulant and pH conditions
- Good control of coagulant dose and pH to maintain optimum conditions particularly during the initial mixing stage. Underdosing of coagulant or inadequate pH control produces poor floc, whilst overdosing increases the quantity of solids for removal and can, in some circumstances, produce large, weak floc that can be difficult to remove efficiently
- Good mixing at the point of chemical dosing to ensure rapid intimate contact between water and coagulant
- Optimisation of flocculation: where mechanical flocculation is used, optimum paddle speeds need to be determined based on performance of the subsequent treatment process
- Avoidance of excessive floc shear after flocculation, which could result from turbulence at weirs, pipe bends or constrictions, and from high flow velocity (above 0.3 m/s)
- Laboratory jar tests are used to select the best combination of coagulation chemicals and pH, which should be verified carefully on the plant

An additional consideration for cyanotoxins is the risk of cell lysis with a high degree of mixing on coagulant addition. Where very high intensity of mixing is generally applied, a compromise may be required between the requirements for effective coagulation and the potential for cell lysis and cyanotoxin release.

Polyelectrolytes are often used in conjunction with metal ion coagulants, primarily as flocculant aids to produce floc which is more easily removed by subsequent clarification or filtration. These are normally added shortly after

coagulant, to provide a lag time for primary floc particles to form. This lag time can be critical to good performance, particularly under cold water conditions, and ideally needs to be established on a site-by-site basis.

SLUDGE AND BACKWASH DISPOSAL

Once confined in sludge of any type, cyanobacteria may lose viability, die, and release dissolved toxin into the surrounding water [6]. This can occur within one day of treatment and can result in very high dissolved toxin concentrations in the sludge supernatant. Similarly, algal cells carried onto sand filters, in flocs or individually, will rapidly lose viability. As a result, if possible, all sludge and sludge supernatant should be isolated from the plant until the toxins have degraded sufficiently. Microcystins are readily biodegradable [7] so this process should take 1-4 weeks. Cylindrospermopsin appears to be slower to degrade [8] and the biological degradation of saxitoxins and anatoxins has not yet been widely studied. However, the saxitoxins are known to be stable for prolonged periods in source water, so caution is recommended.

During a bloom where some cells are carried through to the filters, backwash frequency will probably increase. This is desirable to reduce the risk of dissolved toxin released into the filtered water. Operators should be aware of the possibility of toxic algae in the backwash water, and consequent risk of elevated dissolved toxin levels.

For more details, follow these links for

Coagulation and flocculation

Clarification

Rapid filtration

MEMBRANE FILTRATION

Membrane processes are becoming an increasingly viable option for treatment of both small supplies and larger sources at risk of microbiological contamination (e.g. *Cryptosporidium*). Membranes used in water treatment can be classified as:

- Microfiltration (MF) membranes for removal of fine particulate material above 1 µm in size, such as *Cryptosporidium* and some bacteria
- Ultrafiltration (UF) membranes for removal of colloidal particles of less than 0.1µm and high molecular weight organics
- Nanofiltration (NF) membranes for removal of lower molecular weight organics, colour and divalent ions such as calcium and sulphate
- Reverse osmosis (RO) membranes for desalination of seawater or brackish water

Generally cyanobacterial cells and/or filaments or colonies can be expected to be 1 micron in size or larger. Therefore membranes with a pore size smaller than this will remove cyanobacterial cells. Figure 5-2 is a representation of the removal efficiency of various filtration processes. As the figure shows, in general, micro- and ultra-filtration membranes could be expected to remove cyanobacterial cells effectively. In reality, pore size distributions will vary between manufacturers, so specific information should be sought regarding pore sizes. Clearly the efficiency of removal will also depend on the integrity of the membranes. Processes such as nanofiltration and reverse osmosis membrane filtration will have a pre-treatment step designed to remove particulates and dissolved organic carbon to minimise fouling of the membranes. Therefore, if the pre-treatment processes are working effectively, only dissolved toxin could be expected to challenge these membranes. In the case of micro- and ultra- filtration, healthy cyanobacterial cells may be concentrated at or near the membrane surface. The extent of damage to the cells will

depend on the flux through the membranes, pressure and the time period between backwashes and removal of the waste streams [9]. As with coagulation, optimisation of the processes is recommended, with frequent backwashing, and isolation of the backwash water from the plant due to the risk of the cells releasing dissolved toxin. Ultra- and micro- filtration membranes cannot be expected to remove dissolved toxins released from damaged cells on the membrane surface. In practice, some removal has been noted. As this is most likely due the adsorption of the toxins onto the membrane surface, it would be expected to vary between membrane materials, and to decrease significantly with time as the adsorption sites are occupied by the toxin molecules.

Submerged membrane systems may offer advantages over pressurised systems for waters with high cyanobacterial concentrations as submerged membranes avoid pumping of the water prior to the membrane, and the pressures applied are much less, hence the potential for cell lysis is reduced. However, this benefit may be offset by greater accumulation of cyanobacterial cells in the membrane tanks of submerged systems. This accumulation might be reduced operationally by draining down the tanks more frequently at times of cyanotoxin risk.

For pressurised systems, potential for cell lysis may be greater for crossflow systems than for dead-end operation, particularly if accumulation of bacterial cells in the recycle stream is allowed to occur.

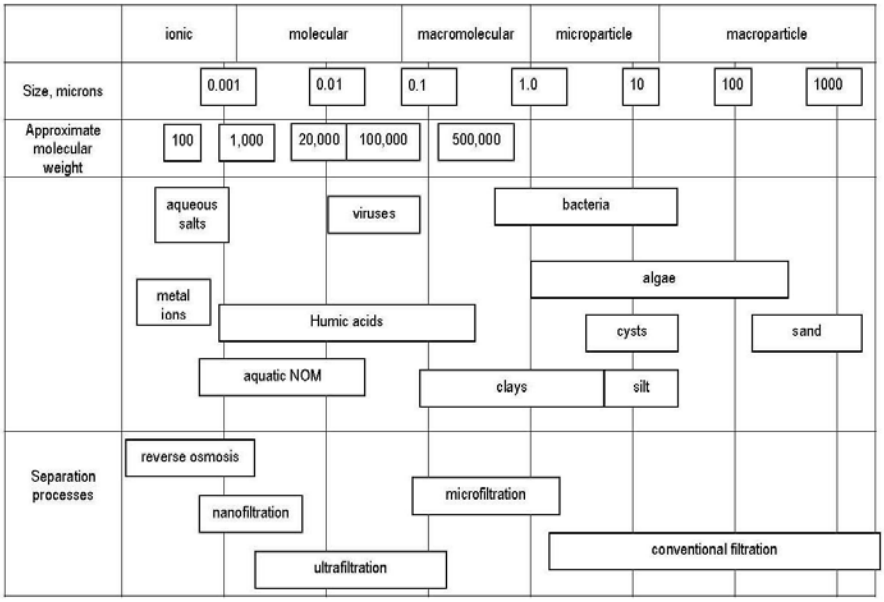

Figure 5-2 Efficiency of various filtration processes

For more details, follow these links:

Membrane modules

Permeate flow rate

Pre-treatments

Monitoring and control

Pressurised or submerged membranes

Dead-end or crossflow

CYANOTOXIN REMOVAL

Even if treatment is aimed at removing cells intact with their intracellular toxins, there is the possibility that dissolved toxins may be present. Thus it is always prudent to send samples for chemical analysis for the toxin most likely to be present. This knowledge will come from a history of observation and monitoring as described in Chapter 3. It is likely that the analysis will take at least 24 hours, possibly more, so it is desirable to initiate treatment measures to remove the maximum level of the toxin most likely to be present.

Processes to remove dissolved microcontaminants, including cyanobacterial toxins from drinking water, are strongly influenced by the properties of the target compound. More details on the structures of cyanobacterial toxins are given in Chapter 1.

As mentioned earlier, conventional treatments such as coagulation etc, are not effective for the removal of dissolved cyanotoxins. The three categories of water treatment processes that can be applied for the effective removal of dissolved toxins are:

- ***Physical processes*** e.g. removal using activated carbon, membranes
- ***Chemical processes*** e.g. oxidation with chlorine, ozone and potassium permanganate
- ***Biological processes*** filtration through sand or granular activated carbon (GAC) supporting a healthy biofilm

PHYSICAL PROCESSES

ACTIVATED CARBON

Activated carbon is a porous material with a very high surface area. The internal surface provides the sites for the target contaminants such as algal toxins to adsorb. Activated carbon is used extensively in water treatment for adsorption of organic contaminants, particularly pesticides, volatile organic compounds, cyanotoxins, and taste and odour compounds, often resulting from algal activity.

Activated carbon is available in two forms, granular activated carbon (GAC) and powdered activated carbon (PAC). Powdered activated carbon can be added before coagulation, during chemical addition, or during the settling stage, prior to sand filtration. It is removed from the water enmeshed in floc during the coagulation and sedimentation process, in the former cases, and through filtration, in the latter. As the name implies, PAC is in particulate form, with a particle size typically between 10 and 100 μm in diameter. PAC is dosed as a slurry into the water, and is removed by subsequent treatment processes. Its use is therefore restricted to works with existing coagulation and rapid gravity filtration, or it may be applied upstream of a membrane process. One of the advantages of PAC is that it can be applied for short periods, when problems arise, then stopped when it is no longer required. With problems that may arise only periodically such as algal toxins, this can be a great cost advantage. A disadvantage with PAC is that it cannot be reused and is disposed to waste with the treatment sludge or backwash water.

Granular activated carbon is used extensively in many countries for the removal of micropollutants such as pesticides, industrial chemicals and tastes and odours. The particle size is larger than that of PAC, usually between 0.4 and 2.5 mm. Granular activated carbon is generally used as a final polishing step, after conventional treatment and before disinfection. It can also be used as a replacement medium for sand and/or anthracite in primary filters. The advantages of GAC are that it provides a constant barrier against unexpected episodes of tastes and odours or toxins, and the large mass of carbon provides a very large surface area. The disadvantage is that it has a limited lifetime, and must be replaced or regenerated when its performance is no longer sufficient to provide high quality drinking water. Filtration through GAC is often used in conjunction with ozone. When used in conjunction with ozone it is sometimes

called BAC, or biological activated carbon; however, this is can be misleading as all GAC filters function as biological filters within a few weeks to months of commissioning.

Follow these links for more information on activated carbon:

Manufacture

Characterisation

The adsorption process

POWDERED ACTIVATED CARBON

APPLICATION OF PAC FOR OPTIMUM PERFORMANCE

One disadvantage with PAC is that the contact time is usually too low to utilise the total adsorption capacity of the carbon. Dosing of PAC immediately before, or during, coagulation may reduce its effectiveness by incorporation into floc, and should be avoided if possible. The PAC can also be applied after coagulation. The advantage of this placement is that a significant proportion of the competing compounds, the natural organic material (NOM), has been removed during the coagulation process. The disadvantage is that the contact time, where the PAC is mixed efficiently through the water, is greatly reduced. There is some evidence that a layer of PAC on top of the conventional filters may provide some additional removal. This has not been shown conclusively for the removal of toxins, so could not be recommended as an effective barrier. Generally, the most suitable place for dosing PAC is upstream of coagulation in a separate PAC contact basin, or in a pipeline where there is some distance between the source water off-take and the treatment plant.

The type of treatment process can also influence PAC performance. Accumulation of PAC in floc blanket clarifiers and filters may give benefits of extending the contact time and PAC concentration. Contact time in DAF cells is relatively short, although long flocculation times could be beneficial.

For a particular site, laboratory tests should be carried out to help evaluate the best position for PAC dosing by simulating the treatment stream, as well as identifying suitable PAC type and dose.

For details of process design for PAC application click here

PAC TYPE AND DOSE REQUIREMENTS

Natural organic material plays a large role in controlling the removal of microcontaminants using activated carbon. The NOM is present in all water sources at much higher concentrations than the target compound. For example, a concentration of 5 $\mu g\ L^{-1}$ of toxin entering a treatment plant would be considered quite high, whereas a concentration of 5 $mg\ L^{-1}$ of dissolved organic carbon (DOC) in surface water would be moderate. In this situation the concentration of NOM (approximately 2 x DOC) [10] is 2000 times that of the target compound, the toxin. Clearly it offers very high competition for adsorption sites on the activated carbon. The difficulty in providing guidelines for the dosing of PAC for the removal of any compound is the overriding influence of the competing NOM. Every water source will have NOM of different concentration and character, and these factors are controlled by site-specific conditions such as vegetation, soil type, climatic conditions etc. As a result, only broad guidelines can be given and, as with the choice of activated carbon, it is suggested doses are determined on a site-specific basis.

Click here for a simple PAC comparative test

The dose recommendations given in the following sections are reliant on operator knowledge of the incoming toxin concentration. In practice toxin analysis undertaken in a qualified laboratory may have a turnaround time of several days. An effective monitoring program as recommended in Chapter 3, together with the application of an Alert Levels Framework described in Chapter 6, should allow water quality managers to estimate the maximum toxin concentration that could be expected to enter the plant. It is prudent to dose assuming the highest probable concentration, then adjust the PAC appropriately when actual concentrations are known.

Click here for a simple PAC dose requirement test

MICROCYSTINS.

Microcystins are relatively large molecules compared with the other toxins. From molecular modelling the size can be approximated to around 1-2 nm, although it is very difficult to estimate the hydrodynamic size of a charged molecule in solution. The charged groups, carboxylic acid groups and arginine amino acids, are hydrophilic (water soluble) groups, whereas the microcystins also have sections that are hydrophobic. In addition the microcystins are in the size range of a large proportion of the NOM competing for adsorption sites on the carbon. The influences on the removal of microcystins by activated carbon are therefore quite complex.

The best activated carbon for the microcystin toxins is a good quality carbon with a high volume of pores in the size range > 1 nm. This type of carbon will also display good kinetic properties. Most wood-based, chemically activated carbons have the desired properties. However, these carbons can be quite expensive, and some coal- or wood-based steam activated carbons also have a reasonably high proportion of larger pores. In the case of microcystins, it is desirable to test several carbons, along with a good quality wood-based carbon, to determine the best one for a particular water quality. If it is not possible to compare carbons for the adsorption of microcystins, the tannin number test, or even the adsorption of DOC, would serve as a good surrogate testing procedure. Once the tests have been completed, it is advisable to do a cost analysis of the carbons to determine which is the best value for money. Simple testing procedures can be found by following the links in the previous section. For example, a more expensive carbon may be the most cost effective if much lower doses are required.

Table 5-1 gives some general recommendations for required doses of PAC when a good quality appropriate carbon is used for the removal of four of the microcystins. The extent of removal by PAC, and therefore the required PAC doses, varies enormously for the microcystins. If microcystins are present in source water, and activated carbon is to be a major process for their removal, it is necessary to determine the variants of microcystins present. Although m-LR is the most common microcystin worldwide, it seldom occurs without other variants also present in the water. It is not uncommon in Australia to find a bloom producing a mix of 50:50 m-LR and mLA. Microcystin LA is as toxic as LR, but is considerably more difficult to remove using PAC. In contrast, mRR is readily removed by PAC, but is considerably less toxic. There are many other microcystins that may be present in source water, but there is no information on the removal of these compounds by PAC.

The presence of a mixture of toxins does not appear to affect the doses, therefore, for a mixture of m-LR and mLA at 1 $\mu g\ L^{-1}$ each for example, add the doses for each toxin individually.

SAXITOXINS.

Saxitoxins are smaller molecules than microcystins, and can be expected to adsorb in smaller pores. As a result of this, carbons with a large volume of pores < 1nm are more effective for these toxins. Good quality steam activated wood, coconut- or coal-based carbons are usually the best. The comparison of activated carbons specifically for the removal of saxitoxins is probably not an option for most water authorities due to the high cost of the analysis. However, as a general rule, carbons that are effective for the removal of tastes and odour compounds MIB and geosmin are also

effective for saxitoxins. When no other test is available, carbons with a high iodine number or surface area of 1000 $m^2 g^{-1}$ or higher may be suitable.

Similar to microcystins, the different variants of the saxitoxins adsorb to different extents on PAC. Fortunately in this case, the most toxic are generally those in the lowest concentration and are removed more readily. In general a dose of 20 to 30 mg L^{-1} and a contact time of approximately 60 minutes would be recommended for an inlet concentration of 10 µg L^{-1} STX equivalents, and a finished water goal concentration of <3 µg L^{-1}.

CYLINDROSPERMOPSIN.

There are very limited data available describing the removal of cylindrospermopsin by activated carbon. The molecular weight of the molecule (415 g mol^{-1}) indicates that it would be removed by carbons similar to those recommended for saxitoxins. However, laboratory results have shown that carbons possessing higher volumes of larger pores are the most effective, suggesting the molecule has a larger hydrodynamic diameter than indicated by its molecular weight [11]. Thus it appears that the carbons that are effective for microcystins are also effective for cylindrospermopsin.

From the limited information available, PAC doses recommended to achieve a target of 1 µg L^{-1} for cylindrospermopsin would be 10-20 mg L^{-1} for an inlet concentration 1-2 µg L^{-1} and 20-30 for an inlet concentration of 3-4µg L^{-1}.

ANATOXIN-A.

The limited data that exists for anatoxin-a removal by PAC suggests that similar removals to that of m-LR can be expected [12].

Table 5-1 gives a summary of the general recommendations for PAC application.

Table 5-1 General recommendations for PAC application in source water with a DOC of 5 mg L^{-1} or less, and contact time 60 minutes *

Toxin		Inlet concentration (µg L^{-1})	PAC dose (mg L^{-1})	Type of PAC
microcystins	m-LR	1-2	12-15	Wood-based, chemically activated, or high mesopore coal, steam activated
		2-4	15-25	
	mLA	1-2	30-50	
		2-4	NR**	
	mYR	1-2	10-15	
		2-4	15-20	
	mRR	1-2	8-10	
		2-4	10-15	
cylindrospermopsin		1-2	10-20	As above
		2-4	20-30	
saxitoxin		5-10 STX eq	30-35	Coal wood or coconut, steam activated

*These doses were estimated from laboratory experiments using the most effective PAC. The actual doses required will depend strongly on water quality and effectiveness of activated carbon. Site and PAC specific testing is recommended

**NR-not recommended

GRANULAR ACTIVATED CARBON

APPLICATION OF GAC

GAC is used in fixed-bed adsorbers, either by conversion of existing rapid gravity filters, or more usually in purpose-built vessels. Flow through the GAC is usually downwards, although upflow designs and fluidised bed reactors are also available.

During GAC filtration, the bed becomes progressively saturated with organics from inlet to outlet, forming an adsorption front within the bed, which moves progressively over time. When the adsorption front reaches the bottom of the bed, the concentration of organics in the water leaving the bed increases, producing the characteristic breakthrough curve. The time taken for breakthrough to occur depends upon the type of GAC used, the concentration and type of organics, and the empty bed contact time (EBCT). A high rate of adsorption (or low velocity of flow) produces a shallow adsorption front, which in turn leads to a sharp breakthrough curve. This is illustrated in Figure 5-3 for the presence of one organic contaminant, where the y-axis is the concentration of the contaminant in the outlet from the filter represented as fraction of inlet concentration (C/C_o), and the x-axis is the number of bed volumes treated. In this case a decision to regenerate or replace the GAC would be made on the goal concentration of the contaminant. Depending on the acceptable concentration range, this may be when the contaminant is first detected ($C/C_o>0$) or a percentage removal (e.g. $C/C_o>0.5$) is achieved. In reality, the situation is far more complex. The major organic component present in the water will be NOM. Where the GAC is used for the minimisation of disinfection by-products, the breakthrough of DOC (or the surrogate UV absorbance at 254 nm) would be of most concern, and this might look similar to Figure 5-3. The decision to replace or regenerate the GAC is therefore relatively straightforward based on the required DOC concentration or removal. However, when the primary treatment objective is the removal of cyanotoxins their transient nature will usually not permit the trending of adsorption as shown in Figure 5-3, and many studies have shown that DOC is a poor predictor of GAC performance for the removal of other organics. In particular, toxins and taste and odour compounds will usually still be effectively removed by GAC while DOC breakthrough is up to 90%, or C/C_o >0.9 [13]. Therefore care should be taken when deciding on the water quality criteria that will drive the replacement or regeneration of the GAC when the primary goal is toxin removal. A suggestion for a simple qualitative monitoring test that may aid in the decision to replace or regenerate GAC is given in the following section.

When the water quality criteria for effluent from the filter are exceeded, GAC is regenerated thermally (reactivated) or replaced. Thermal reactivation requires removal of the GAC from the adsorber and transport to the regeneration facility. The GAC is then heated in a special furnace to progressively higher temperatures. During the heating phases the following occur: drying of the GAC and desorption of volatile organics; carbonisation of non-volatile organics to form ‘char’ and finally gasification of the ‘char’. Accurate control of heating is essential if the correct pore structure is to be maintained and excessive loss of carbon avoided.

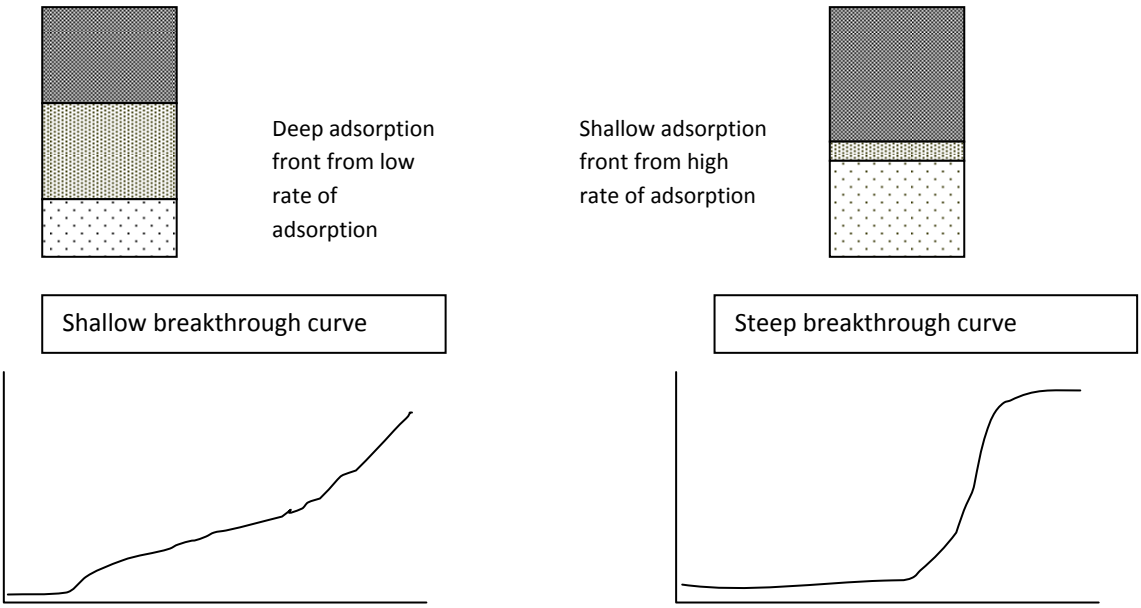

Figure 5-3 Effect of the adsorption front on the shape of the breakthrough curve

Factors which affect the performance of GAC for removal of organic compounds are:

- the capacity of a particular carbon for the organic compound(s) in question
- the contact time between the water and the carbon
- the concentration of the organic compound in the feed, and the desired removal
- the presence of NOM which will compete for adsorption sites

All GAC adsorbers develop biological characteristics to a greater or lesser extent, particularly when treating surface waters at higher water temperature. Biological characteristics can be enhanced by pre-ozonation and longer EBCTs, and can provide some advantages such as:

- removal of biodegradable organics produces a more biologically stable water to reduce the potential for detrimental biological growth in the distribution system
- enhanced removal and extended bed life, even for apparently refractory organics (e.g. pesticides) because of biodegradation of adsorbed compounds
- potential for ammonia removal
- removal of biodegradable ozonation by-products such as aldehydes and ketones, (even at relatively short EBCT)

Benefits from biological effects will diminish at water temperatures below 10C or EBCT below 10 minutes. The disadvantage of biological activity is extensive biomass growth in the bed which increases the need for backwashing. This may reduce the life of the GAC, or result in increased attrition due to physical breakdown of the particles.

More information about monitoring and control of GAC processes, including determination of regeneration frequency, can be found here

TYPES OF GAC

As with PAC, the ability of the adsorbent to remove the toxins depends on the raw materials, method and extent of activation, a range of other surface characteristics, and the toxin's physical characteristics. Before a particular GAC is chosen, a comparative test can be undertaken to determine the most effective GAC for the particular toxin, or the mixture of toxins for which a plant must be prepared.

Click here for a simple GAC comparative test.

Click here for more general guidance on selection of GAC

LIFETIME OF GAC

The service life of the bed is dependent on the capacity of the carbon used, the empty bed contact time (EBCT) or any physical breakdown caused by frequent backwashing.

Click here for more information on EBCT

There are a number of tests designed to predict breakthrough of microcontaminants on GAC, and some of these have been reasonably successful when used for microcontaminants that are present in the water constantly. However, there are two main reasons why these tests should be treated with caution when applied for the prediction of toxin breakthrough:

Transient nature of the problem Toxins are rarely constantly present in source water; the problem is of a transient nature, often appearing regularly in a particular season each year. In most cases the life of the GAC is controlled by the adsorption of the wide range of organic compounds in NOM, which is present year-round. A short-term laboratory test to determine the removal capacity for toxins will not give an accurate estimate of the length of time GAC can be expected to remove occasional episodes of the contaminants.

Biological degradation Microcystins and cylindrospermopsin are readily biodegradable under certain conditions. If a GAC filter is consistently degrading the toxins, the lifetime could be indefinite. Or, more likely, the GAC filter may initially allow some breakthrough of the compounds, and then the biological function of the filter could "cut-in" resulting in no toxins detected in the outlet water. In the absence of the toxins the biological filter may lose the ability to degrade the compounds, and allow breakthrough during the following toxic challenge

Recent research by the Australian Water Quality Centre has shown that the less problematic, low toxicity saxitoxins can be converted to the more toxic variants during biological activity on an anthracite biofilter. This leads to the disturbing possibility that the water can be rendered more toxic after dual media filtration in a conventional plant [14].

Although it is very difficult to accurately predict the "*lifetime"* of GAC for the removal of toxins, it is recommended that a filter be tested, or monitored, for removal, if this is to be a major barrier to algal toxins entering the distribution system. This type of testing can give an estimate of the ability of the GAC *at the time* to remove the toxins, but cannot predict *how much longer* it will effectively remove the compounds.

Click here for a simple monitoring test for GAC

Although the use of GAC for toxin removal is very complex, some general suggestions can be given based on pilot and laboratory scale studies for microcystins and saxitoxins. No data exists for the long term removal of cylindrospermopsin by GAC. Recommendations for microcystins could also be applied for cylindrospermopsin until more information is available.

MICROCYSTINS AND CYLINDROSPERMOPSIN.

Reports of length of time until breakthrough vary for microcystins, but would be expected to be between 3 and 12 months from commissioning if the filter is challenged with the toxins on an intermittent basis.

SAXITOXINS.

Saxitoxins appear to be well removed by GAC, and good removals (up to 75% removal of toxicity) have been reported after 12 months of running laboratory scale GAC columns [15].

ANATOXIN-A.

Similar to PAC, the limited data that exists for anatoxin-a removal by GAC suggests that similar removals to that of m-LR can be expected [12].

For more detailed information on GAC specifications, testing and filtration process design, refer to BEST PRACTICE GUIDANCE FOR MANAGEMENT OF CYANOTOXINS IN WATER SUPPLIES. EU project "Barriers against cyanotoxins in drinking water" ("TOXIC" EVK1-CT-2002-00107)

MEMBRANE FILTRATION

Membranes are physical filtration barriers, and the main factor influencing removal of microcontaminants is the size, or hydrodynamic diameter, of the compound compared with the pore size distribution of the membrane. Other factors, such as electrostatic interactions and a buildup of NOM and particles on the membrane (membrane fouling) can also alter the permeability of the membranes to particular compounds. However these factors are very difficult to predict, and cannot be taken into account for cyanotoxin removal. Figure 5-1 shows the approximate ranges of pore size of common membranes, and molecular weight and size of the compounds and particles they can reject. According to Figure 5-1, microcystins should be rejected by RO membranes and nanofiltration membranes with a pore size distribution in the lower range. Saxitoxins, anatoxins and cylindrospermopsin could also be expected to be removed by RO. However, according to this figure, even RO membranes may allow the smaller toxin molecules to permeate the membrane. The crucial issues are the pore size distribution of the particular membrane, which should be available from the manufacturer, and the integrity of the membrane. As mentioned earlier, membranes contain a range of pores, and larger pores could allow the molecules to permeate.

More operational information about membranes can be found here

CHEMICAL PROCESSES

Most oxidants used in water treatment have the ability to react with cyanobacterial toxins to varying degrees and this depends on type of oxidant, dose and the structure of the toxin.

CHLORINE

Chlorine is an oxidant which will react with many organic compounds, including algal toxins and NOM. The most reactive form of chlorine is hypochlorous acid (HOCl), which is in equilibrium with the hypochlorite ion (OCl^-) in solution. The chemical equation is given below.

$HOCl \Leftrightarrow H^+ + OCl^-$

The concentration of hypochlorous acid is dependent on the pH of the water. An example of the relative concentrations of the two major forms of chlorine over a moderate range of pH is given in Table 5-2. From the table it can be seen that a small change in pH can result in a large change in the concentration of the most reactive form, therefore the reaction of chlorine with any compound will be dependent on pH.

Table 5-2 Ratio of HOCl to OCl^- and concentrations of the species at different pH. Initial concentration 5.4 mg L^{-1} as Cl_2

pH	6.0	6.5	7.0	7.5	8.0	8.5	9.0
HOCl:OCl^-	32:1	10:1	3.2:1	1:1	0.32:1	0.1:1	0.03:1
HOCl (mg L^{-1})	3.9	3.6	2.9	2.0	1.1	0.4	0.1
$^-$OCl (mg L^{-1})	0.1	0.4	1.1	2.0	2.9	3.6	3.9

Chlorine reacts rapidly with a range of molecules, depending on their molecular structure and susceptibility to oxidation. In the presence of NOM, the concentration of chlorine decreases rapidly as a result of reaction with the complex organic mixture comprising NOM. When we use chlorine for the removal of algal toxins we should be aware that a competitive effect is produced between the different types of NOM and the toxins. Some molecules, or structures within molecules are more reactive than others and the rates of reaction between chlorine and organic compounds will depend on their structure. The result of these effects is a large variation in rate and extent of chlorine decay in different waters. As NOM is a complex mixture of organic molecules of unknown character it is very difficult to predict the competitive effect between the reaction of chlorine with NOM and the toxins. To take into account this the concept of chlorine exposure, or CT (concentration x time) is introduced to help describe the reaction of the available chlorine with microcontaminants such as toxins. The CT value is the area under a plot of chlorine residual vs time, and describes the amount of free chlorine to which the solution has been exposed. A description of the CT concept for disinfection can be found in the Australian Drinking Water Guidelines [16].

MICROCYSTINS

Microcystins are fairly reactive with chlorine. They have a conjugated double bond in their structure which is susceptible to chlorine, as well as reactive amino acid groups. As these amino acid groups vary with the type of microcystins, the toxins themselves vary in their reactivity [17]. Of the four most common microcystins, the ease of oxidation by chlorine is given by:

mYR>mRR>m-LR>mLA.

As a general rule the oxidation of all microcystins to below the guideline value will be achieved under the conditions outlined in the general considerations section, below.

SAXITOXINS

Saxitoxins are not as reactive with chlorine as microcystins as their structures do not contain very reactive sites. However, recent work has shown that chlorine is an effective process in the multi-barrier approach to saxitoxin removal, with CT values of 20 mg min L^{-1} producing up to 90% removal at pH between 6.5 and 8.5 [3].

CYLINDROSPERMOPSIN

The limited data available on the chlorination of cylindrospermopsin suggests it is more susceptible to chlorination than microcystins [18]. The conditions outlined above for the chlorination of microcystins are also applicable for cylindrospermopsin.

ANATOXIN-A

Anatoxin-a is not susceptible to chlorination [12].

GENERAL RECOMMENDATIONS

Oxidation conditions for microcystins, saxitoxins and cylindrospermopsin**:**

- pH <8
- Residual >0.5 mg L^{-1} after 30 minutes contact
- Chlorine dose > 3 mg L^{-1}
- CT values in the order of 20 mg min L^{-1}

Destruction of the toxins could be expected to range between almost 100% for cylindrospermopsin and the more susceptible microcystins to approximately 70% for saxitoxins.

CHLORINE DIOXIDE

Not effective with doses used in drinking water treatment [19].

CHLORAMINES

Chloramine is a much weaker oxidant than either chlorine or ozone, and only very high doses and long contact times have been shown to have any effect on microcystin concentration [20]. The limited data available for the other toxins indicate that chloramination could not be considered as an effective barrier for the toxins.

OZONE AND OZONE/PEROXIDE

Ozone, like chlorine, is an oxidant. It is extremely reactive and, also like chlorine, is present in water in more than one form. The ozone molecule (structure of three oxygen atoms O_3) reacts with organic molecules present in the water. It also breaks down spontaneously - auto-decomposes - to produce hydroxyl radicals. This is a very reactive chemical species, and it is not discriminating in the structures it attacks. The formation of hydroxyl radicals is dependent on pH, and predominates at pH>8. The decomposition of ozone, formation of hydroxyl radicals, and the reactions of both species with NOM can be described as a chain reaction where NOM plays a part as both an initiator and inhibitor in the formation of hydroxyl radicals [21]. For ozonation the alkalinity of the water is also important, as the carbonate ion plays a strong role inhibiting the formation of the hydroxyl radicals. Therefore, while high alkalinity water may maintain an ozone residual for longer, this is at the expense of the formation of hydroxyl radicals, the most reactive species. When ozone is used in combination with hydrogen peroxide the formation of hydroxyl radicals is increased, and therefore the oxidising potential of the treatment is increased.

MICROCYSTINS

As mentioned above, microcystins have structures present in the molecule that are susceptible to oxidation, therefore the ozone molecule will react with them. In addition, the hydroxyl radical would be expected to react strongly with the microcystins [22]. There is a competitive effect with NOM, always at higher concentration than the toxins, as it can be expected that there will be some sites present in NOM that are as reactive as those on the microcystin molecule.

Similar to chlorine, the reduction in the concentration of microcystins will also depend on the initial dose, but it appears from laboratory and pilot scale work that the maintenance of a residual of 0.3 mg L^{-1} for at least 5 minutes will result in the reduction of microcystins to below detection (by HPLC) in most waters. Water with DOC higher than 5 mg L^{-1} may require higher doses.

SAXITOXINS

As mentioned above, saxitoxins are not as susceptible to oxidation as the microcystins, and are not readily removed by ozonation [23]. An increase in pH, with a consequent increase in hydroxyl radical formation may result in higher levels of removal, but this has not been proven in the laboratory or pilot plant. Conditions suggested for microcystin, above, could be expected to reduce the concentration of saxitoxins by no more than 20%, according to laboratory scale experiments.

CYLINDROSPERMOPSIN

The limited data existing on the ozonation of cylindrospermopsin suggests that the conditions recommended for microcystin will also apply for the removal of cylindrospermopsin [23].

ANATOXIN-A.

Application of ozone as for microcystins will result in significant oxidation of anatoxin-a [24].

GENERAL RECOMMENDATIONS

OXIDATION CONDITIONS FOR MICROCYSTINS, ANATOXIN-A AND CYLINDROSPERMOPSIN

- pH > 7
- Residual >0.3 mg L^{-1} for at least 5 minutes contact
- CT values in the order of 1.0 mg min L^{-1} have been shown to be effective

SAXITOXINS

Ozonation is not recommended as a major treatment barrier

For a description of the ozonation process, follow this link

POTASSIUM PERMANGANATE

Potassium permanganate has been shown to reduce the concentration of microcystins and anatoxin-a considerably [25] and may also be effective for the reduction of cylindrospermopsin [26]. If potassium permanganate application is practised to control manganese it should be maintained in the presence of these toxins. Unfortunately, the data currently available is not sufficient to allow recommendations for dose requirements or to allow us to consider potassium permanganate as an effective barrier.

For a description of the application of potassium permanganate and some laboratory results follow this link

UV AND UV/HYDROGEN PEROXIDE

Ultraviolet irradiation is capable of degrading microcystin-LR and cylindrospermopsin, but only at impractically high doses or in the presence of a catalyst such as titanium dioxide or to a lesser extent cyanobacterial pigments [27, 28]. As with ozone, the presence of hydrogen peroxide promotes the formation of hydroxyl radicals, and increases the oxidising potential of the UV treatment.

For some laboratory results click here

HYDROGEN PEROXIDE

Hydrogen peroxide is not effective on its own. In combination with ozone or UV it produces hydroxyl radicals that are very strong oxidising agents. Insufficient information exists to recommend doses

MORE INFORMATION ON OXIDATION

Reaction rates

Modelling of oxidant processes

BIOLOGICAL PROCESSES

Microcystin variants and cylindrospermopsin show great potential for significant biological removal, even at flow rates approaching those encountered in rapid sand filters [29]. All GAC filters function as biological filters after a few weeks of commissioning so also have the potential of eliminating toxins that are susceptible to biological degradation. Figure 5-4 shows the abundant and diverse biofilm present on sand from a rapid sand filter in a conventional treatment plant. This filter has been functioning as an effective biofilter for the removal of taste and odour compounds for many years.

Only particular strains of certain microorganisms are capable of degrading algal toxins, and sufficient numbers must be present on the biological filters to result in biological removal. In addition, both microcystins and cylindrospermopsin display a “lag phase” between the time the toxin enters the filter, and when the biofilm begins to remove the toxins. That is, the biofilm is said to require time for “acclimation” to the compounds. Knowledge of the origin of the lag phase, and the ability to eliminate it is essential before biological removal can be confidently relied upon as an effective barrier against these toxins. If the presence of toxins in sand filters is a common occurrence, it is possible that some biological removal will take place. However, if pre-filter chlorination is practised as a means of reducing particle counts, it is very unlikely that sufficient biological activity will be maintained for toxin removal. As a

result of these issues, biological filtration cannot be considered an effective barrier to cyanotoxins at present. However, slow sand filtration and bank infiltration, practised in some European countries, are processes where very long contact times and high biological activity result in excellent removal of taste and odour compounds and microcystins [4]. There is also good preliminary evidence that these processes will be effective for cylindrospermopsin removal.

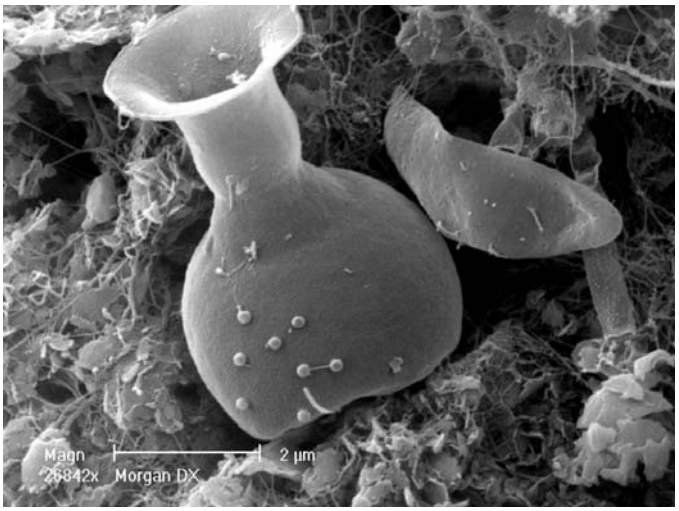

Figure 5-4 Scanning electron micrograph of biofilm on a sand particle from the rapid sand filter at Morgan Water Filtration plant, South Australia

For more information on riverbank and slow sand filtration, click here

CHAPTER 5 TREATMENT OPTIONS (LEVEL 2)

CYANOBACTERIA CELL REMOVAL

MICROSTRAINERS

GENERAL CONSIDERATIONS

The essential features of a microstrainer, illustrated in Figure 5-1(L2) are:

- the drum, generally between 1.5 to 3 m in diameter and up to 5 m long with a variable speed drive
- fabric of either stainless steel mesh or polyester cloth with apertures normally in the range 20 - 40 µm for microstraining or larger (e.g. 1 mm) for fine screening. The fabric is normally attached to small frames fixed to the drum, which can be removed individually without draining down
- wash water jet arrangement with a trough for collecting screenings
- a tank in which the microstrainer is housed (usually concrete) consisting of an inlet chamber with a weir for water to flow into the interior of the drum and an outer chamber containing the drum itself with an outlet weir

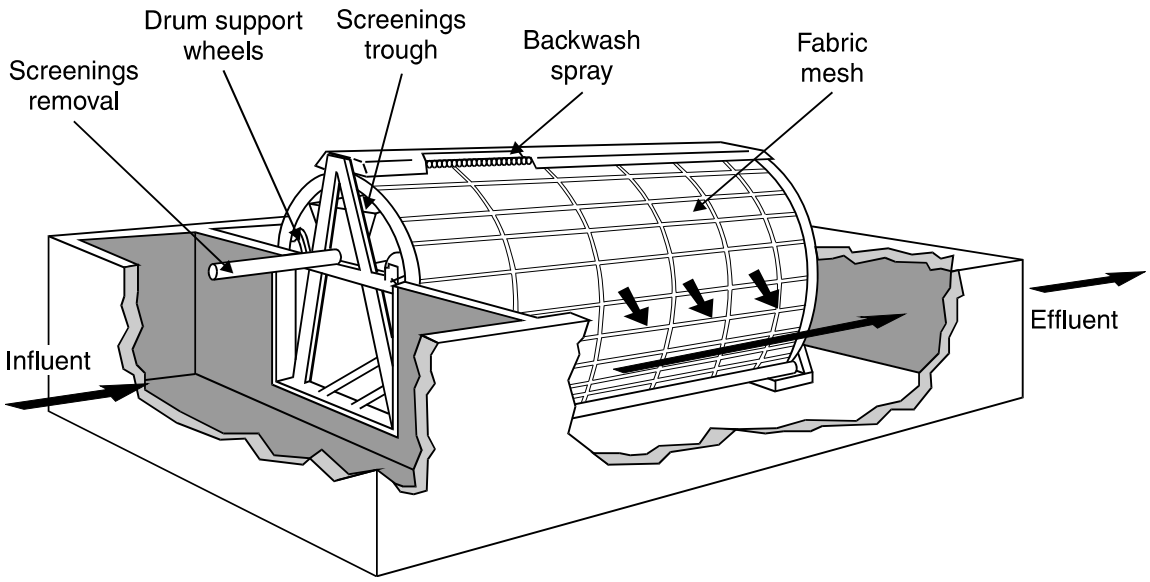

Figure 5-1(L2) Microstrainer

The main factors influencing performance are:

- speed of rotation. This will depend on solids loading. If solids loading increases, the fabric will block more quickly, and intensity of cleaning needs to be increased. This is achieved by increasing drum rotational speed. Drums usually operate up to a top speed of about 5 rpm;
- washing, which must be effective otherwise headloss across the fabric will be excessive. The maximum headloss is typically 0.3 m. The wash water demand is between 1 and 3% of the volume treated;
- sodium hypochlorite washing or ultraviolet irradiation to prevent blinding of the fabric by algae or a zoogloeal film. If build-up of calcium carbonate scale occurs, acid washing may also be necessary.

PROCESS MONITORING AND CONTROL

The only control variable is headloss which is controlled by varying the rotational speed of the drum. Headloss across the fabric is measured using a differential pressure cell or electrodes to determine water levels. The variable speed motor can be controlled automatically based on the signal from this cell.

Return to level 1

RIVERBANK, SLOW SAND AND BIOLOGICAL FILTRATION

PROCESS MONITORING AND CONTROL

The main parameters used for monitoring slow sand filters are flow rate, headloss and filtrate turbidity. Good operational practice for these parameters should also provide good performance for algal removal.

Filtration rate is controlled by means of a valve on the filter outlet. As the filter becomes blocked and headloss across the filter increases, the outlet valve must be progressively opened to allow the same filtration rate with a constant head above the sand. Valve adjustment can be manual on a daily basis (because headloss builds up slowly) or automatic, based on a signal from flow metering equipment. Headloss can be monitored using differential pressure cells, or measured manually using level indicating tubes. Data from headloss measurement can be used to predict when skimming of a bed will be necessary, and assist planning of works operation to minimise the number of filters out of use at any one time.

For river bank filtration sites monitoring of filtrate turbidity will yield information on the system's performance concerning particle removal. However, it needs to be taken into account that elevated turbidity and also increasing headloss may also result from processes in the groundwater body surrounding the well (physical or bio-chemical well-clogging). Monitoring of source water quality and determination of the nature of the particles encountered can help identify the cause.

PERFORMANCE OPTIMISATION FOR ALGAE REMOVAL

The following recommendations relate mainly to slow sand filter works with primary rapid gravity filtration. Works without primary filters may need a more conservative operating regime, for example in relation to maximum filtration rates and start-up conditions.

1) Slow sand filters typically contain a minimum of 300 mm depth of sand with an effective size of 0.3 mm (tolerance ±10%) and a uniformity coefficient of 1.7-2.3. All sources of new sand must be assessed for quality and grading before purchase. Sand removed during the cleaning process is usually washed on site to agreed quality (silt/particulate organic carbon) and grading specification. Only washed sand can be reused for resanding or rebuilding.

2) Filtration rate: slow sand filters may be operated within a band of 0.05-0.5 m h^{-1} (m^3 m^2 h^{-1}) downflow, although in practice the normal rate is narrower at 0.1-0.4 m h^{-1}. Pretreatment may be needed to achieve high filtration rates without excessive headloss build-up.

3) Where the level of sand in the filter has fallen to 300 mm, a decision needs to be made as to whether to top up the bed with clean media ("resand") or to replace the lower layers with clean media ("rebuild"). This decision is based on a number of factors, the main factor being the cleanliness of the sand in the bed. If the lower levels of sand accumulate a large mass of material, then the starting head loss may be high and the run

length short. Historically, dirty sand in the lower layers has not given rise to particle breakthrough although water quality can be adversely affected in terms of low dissolved oxygen and excessive growth of undesirable biological populations in the underdrains.

4) Following resanding or rebuilding, the bed is either run to waste or recycled, at a minimum flow rate of typically 0.025 m h^{-1}, until filtered water quality targets are met e.g. coliforms/*E. coli* below 100/10 per 100 ml.

5) During periods of increased cyanotoxin risk, consideration should be given to the possibility that the sand washwater may contain high concentrations of extracellular cyanotoxin because of cell lysis. Recycle should therefore be avoided if possible.

PERFORMANCE OPTIMISATION FOR TOXIN REMOVAL

The few parameters that can be optimised in bank filtration settings are the share of surface water compared to ambient groundwater (share of bank filtrate) and the minimum travel time of the bank filtrate in the subsurface. Both parameters depend on the distance from river to well and the pumping rate for a given hydro-geological setting. Simulation models (e.g. analytical/numerical GW models) can assist to determine the share of bank filtrate and the travel time for a given setting (e.g. BFS, MODFLOW, FEFLOW).

In order to assess the necessary travel time, it needs to be taken into account that under optimal conditions extra-cellular microcystin is usually well bio-degradable (half-lives may lie in the range of hours). However, in environments without an adapted microbial community, lag phases of up to one week may occur before degradation commences.

The following pre-requisites are postulated for sufficient removal of microcystin to < 1 µg L^{-1} by bank filtration at source waters with frequent cyanobacterial blooms (i.e. adapted microbial population):

- extra-cellular microcystin < 50 µg L^{-1},
- middle to fine grained sandy aquifer,
- aerobic conditions
- temperatures > 15 °C,
- residence times > 7 d (see figure 1)

For suboptimal conditions, residence times need to be much higher (> 70 d).

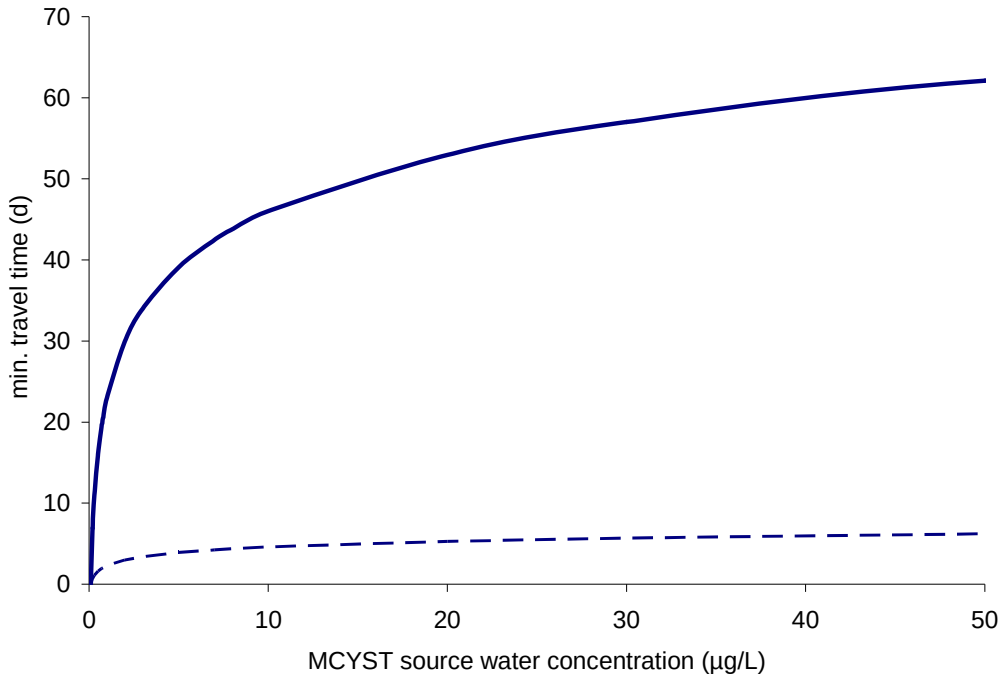

Figure 5-2(L2) Minimum subsurface travel time for sufficient removal of microcystin depending on source water concentration of extra-cellular microcystin for a) worst-case conditions (solid line), i.e. anoxic/anaerobic conditions, temperature < 15°C, and b) optimal conditions (dashed line).

Recent investigations have shown that for cylindrospermopsin biodegradation rates are similar to those determined for microcystin though their extra-cellular toxin share might be generally higher.

Return to level 1 (cyanobacteria removal)

Return to level 1 (cyanotoxin removal)

CONVENTIONAL TREATMENT

COAGULATION AND FLOCCULATION

PROCESS MONITORING AND CONTROL

Coagulation control is based on maintaining optimum doses and pH for effective algae removal as feed water quality varies. Automatic control requires flow proportional control of chemicals, with trimming to the optimum carried out by one of the following methods:

a) Feedback loop control from flocculated water characteristics. Proprietary systems (e.g. Streaming Current Detector) are available to control coagulant dose. Separate control of pH is usually necessary.

b) Feedback loop control based on product water quality from subsequent treatment processes, using signals from pH, turbidity, residual coagulant or colour monitoring instruments. This can require the successful operation of several instruments, depending on treatment requirements.

c) Feedforward control from feed water quality using empirical equations developed from historical data. Enough data are required to confidently relate required dose to quality which will limit its application for most sites. This method may also depend on the successful operation of several instruments, although UV absorbance is often used as the main on-line control parameter.

Methods (b) and (c) can be used as the basis for manual control, with operators regularly taking instrument readings and making appropriate adjustments to doses.

The success of any coagulation control strategy can be dependent on the hydraulic retention time in subsequent treatment. Long retention time systems can be more difficult to control by feedback from product water quality, but are less sensitive to short periods of non-optimum dosing.

PERFORMANCE OPTIMISATION FOR ALGAE REMOVAL

1) Jar tests should be carried out at suitable intervals, initially to identify relationships between coagulation conditions (dose and pH) and raw water quality, and subsequently to check that this relationship does not change with time. The required frequency for this will be site-specific, depending on the variability in raw water quality. It may also be valuable to use jar tests to compare alternative coagulants, to identify the most suitable for a particular site and conditions. Jar tests should be carried out on freshly collected samples, and at the same temperature as the raw water.
2) To maximise algal removal, jar tests need to be carried out on waters with high algal concentrations and appropriate algal counts carried out. However, this will not always be possible, and optimisation for removal of colour or UV absorbance at 254 nm (UV254) in filtered samples may give a working approximation of the requirements for good algae removal. This would need to be confirmed, however, at times of high algal concentrations.
3) Other important parameters in the jar test are total coagulant metal ion concentration and turbidity in the settled water, and soluble metal ion concentration in a filtered sample. Insoluble coagulant metal ion concentration is an indicator of settleability of the floc, and soluble metal ion concentration an indicator of the suitability of the chemical conditions.

Procedures are needed to ensure that operators maintain suitable dosing/pH conditions, identified from jar tests, with varying raw water quality. This can be particularly important for sites where sudden changes in raw water quality can occur, such as for direct river abstraction. Recommended ways of achieving this are outlined below.

- Provide graphs or tables, based on historical data, to relate dose/pH to raw water quality (rather than rely solely on operator experience in this).
- Initiate a program of jar tests initially to obtain data with which to check the validity of these graphs and tables, and then to ensure that the relationship between water quality and coagulation conditions does not change with time.
- Sampling of flocculated water (or coagulated water if this is not available) and measurement of appropriate parameters can provide a check that correct dosing conditions are being applied. Suitable procedures will need to be defined for this. For example it might be beneficial to provide a short period of stirring with a jar tester to establish a reproducible degree of flocculation. Appropriate parameters for measurement are insoluble coagulant metal ion and turbidity in settled samples (settleability of the floc), and colour, UV254 and soluble metal ion in filtered samples (coagulation chemistry). Target values for these will need to be identified on a site-by-site basis.

- The coagulant dose and pH can be checked by sampling and analysing the coagulated water. Polyelectrolyte doses should be checked by volumetric calibration.
- Measurement of turbidity/total coagulant metal ion concentration in clarified water, and colour/UV254 /coagulant metal ion concentration in works filtered water, would also give indications of the performance of coagulation. However, when raw water conditions are changing, there would be a time lag to take into account between coagulation and sampling. The performance of the solids-liquid separation, particularly for clarification, would also need to be taken into account.
- Sampling of clarified water for measurement of total metal ion coagulant and turbidity can give an indication of the success of the coagulation conditions in producing a readily separable floc. Turbidity above 2 NTU, Al above 0.5 mg L^{-1} or Fe above 1 mg L^{-1} would indicate scope for improvement in solids-liquid separation, which might be achieved by attention to coagulation conditions, and perhaps through the use of polyelectrolyte flocculant aid.

If filtered jar test samples appear to show better performance for colour and UV254 removal than that given on the plant for the same coagulation conditions, attention should be given to the initial chemical dosing and mixing conditions on the plant, as these may provide inadequate dispersion for the achievement of good coagulation chemistry. Similarly, if settled samples of flocculated water from the plant (or coagulated water if flocculated samples are not available) have markedly higher turbidity or total coagulant metal ion concentration than jar test samples, this could indicate a limitation in the plant coagulation or flocculation conditions to produce readily settleable floc. Attention should be given to mixing conditions on the plant, or the potential for polyelectrolyte to improve settleability.

Return to level 1

CLARIFICATION

GENERAL CONSIDERATIONS

Clarification processes involve either settling or flotation of the flocculated water. The objective of clarification is to reduce solids loadings to subsequent filters, thereby maximising run times and minimising the risk of breakthrough of particulates, including algae. This is achieved by operating clarification processes to prevent carry-over of solids, based on clarified water quality. The effectiveness of clarification is dependent upon achieving good chemical coagulation, and is influenced by hydraulic and solids loading rates. Ineffective desludging of clarifiers can also cause deterioration in clarified water quality because of carry-over of solids.

Well-operated clarification processes can therefore maximise removal of algal cells and associated cyanotoxin, but there is no evidence of any benefits for extracellular toxin. Biological activity in sludges held within clarifiers could potentially result in algal cell lysis and release of cyanotoxin. Effective sludge removal is therefore important to minimise risk from cyanotoxins.

Generally, clarification would be expected to remove at least 70-90% of the coagulant floc, and therefore give similar removal of algal cells provided these are effectively incorporated into floc by efficient coagulation. Some algal genera containing gas vacuoles (e.g. *Microcystis*) may be removed more effectively by flotation compared with settling.

The information provided in this manual relates to conventional clarification processes. There are many relatively new high-rate proprietary clarification processes available, and some of the principles discussed below would apply to these as well as the conventional processes.

PROCESS MONITORING AND CONTROL

Although good control of chemical coagulation is essential, floc blanket clarification can handle short periods of non-optimum dosing because of the long hydraulic retention times within the process. However, these long retention times can make good feedback control based on product water quality difficult to establish, as a result of long delay times between dose adjustment and effect on product quality.

Periodic removal of sludge from the floc blanket can be controlled based on blanket height by means of optical detector systems suspended in the tanks. Similar systems may allow control based on blanket solids concentration, particularly for use on the recirculation type systems. Desludging of concentrator cones can be controlled by weight of sludge accumulated in the cone.

Control of dissolved air flotation (DAF) is based largely on achieving and maintaining suitable chemical dosing conditions. Other operating variables e.g. air supply, scraper speed, etc. can be optimised once satisfactory chemical dosing has been achieved, and responses to changing raw water conditions can be made by manual adjustments. It may also be possible to implement automatic control by means of a feedback loop based on treated water quality. The latter can be more efficient for DAF than for processes that have a longer retention time.

PERFORMANCE OPTIMISATION FOR ALGAE REMOVAL

1) Ensure that suitable coagulation conditions are maintained not only to maintain good incorporation of particles into floc, but also to produce floc which is readily separable in clarification processes. Measurement of turbidity and coagulant metal ion concentrations in supernatant from settlement jar tests can be used to compare the relative performance of different coagulation conditions in terms of floc settleability. For DAF, the use of flotation jar tests, whilst not critical, would probably give more representative results.

2) Solids removal performance of individual clarifiers should be monitored using turbidity and insoluble coagulant metal ion concentration. Whilst target values need to be set for individual sites, turbidity above 2 NTU, insoluble Al above 0.5 mg L^{-1} or Fe above 1 mg L^{-1} would usually indicate scope for improvement in solids-liquid separation, which might be achieved by attention to coagulation conditions, and perhaps through the use of polyelectrolyte flocculant aid. However, if jar tests appear to give readily separable floc, the problem may lie in the plant hydraulic and mixing conditions.

3) This could be checked by taking samples of coagulated water directly from the plant, and carrying out settling or flotation tests with these samples. These should include periods of flocculation for the coagulated water. If the water quality (turbidity or total coagulant metal ion concentration) from these tests is better than that of the works clarified water, then attention should be given to works flocculation and solids-liquid separation, and the following should be investigated:

    - flocculation performance
    - hydraulic loadings and flow distribution in and between clarifier units
    - floc blanket depth and concentration
    - quantity of air supply to DAF (recycling ratio and saturator pressure)
    - relative performance of individual units

4) Assess whether any uneven flow distribution between units may be influencing the performance of individual units. Check also for any indications of uneven flows within units.

5) Take samples of floc blanket, if possible, and check the concentration as the settled volume after 30 minutes settlement. This should be around 15 - 20% of the original volume. Blanket depth should also be monitored

routinely to avoid any potential for overflow of the blanket into the clarified water launders. There may be scope to increase the frequency of sludge bleed to reduce variations in blanket depth.

6) DAF air supply should be estimated from suppliers' data (based on pressure and water temperature). With a packed saturator, a pressure of between 50 and 60 psi (350 and 450 kPa) and a recycle rate of 7% to 8% would correspond to a dose of between 8 and 10 g air per m^3 water treated. Lower doses than this may limit performance. Higher doses may be causing unnecessary turbulence.

7) Visual inspection of the DAF tanks should identify whether good dispersion of the bubbles across the width of the tank is being achieved, and that the "milky" appearance indicative of effective bubble generation is being achieved.

8) After start-up, avoid sudden changes in flow rate to either floc blanket clarification or DAF.

9) Any attempts to improve clarifier performance should be accompanied by appropriate monitoring of the filters, to identify the knock-on effects on filtered water quality and headloss build-up.

Return to level 1

RAPID FILTRATION

GENERAL CONSIDERATIONS

Generally, the aim is to operate the filters at the highest possible rate less than the maximum design loading, whilst maintaining acceptable filtered water quality for as long as possible between backwashing. However, for algal removal there is an additional consideration of accumulation of algal cells in filters, with the risk of cell lysis and the release of toxin into the filtered water.

The main performance criteria are filtrate quality, run length and headloss. The operational factors which influence performance are given below.

For general guidelines on filter operation the reader is directed to Logsdon et al. [30].

COAGULANT DOSING AND PH CONTROL

Coagulant dose and pH must be optimised for good performance. Dosing less than the predicted optimum reduces the "filterability" of the floc and hence reduces run length even though solids loading is reduced. Dosing more than the predicted optimum simply increases the solids loading onto the filters and consequently decreases run length. Metal ion coagulant can be partially substituted by a cationic polyelectrolyte coagulant, which, for direct filtration (without prior clarification) reduces solids loading to the filters and increases run length. Polyelectrolyte flocculant aids can also be dosed to increase run length.

FILTRATION RATE, FLOWRATE CHANGES AND START-UP

Filtration rates (volumetric flowrate per unit area of filter bed) are typically in the range 4 m per hour to 12 m per hour for conventional filtration applications. The effect of increasing filtration rate is to shorten filter run length. Higher filtration rates are possible if coarser media is used. To compensate for poorer filtration when using coarser media, deeper beds are used; typically the bed depth is 800 to 1200 times the particle diameter. The use of polyelectrolyte flocculant may also be beneficial when using coarser media.

Filter performance can be sensitive to changes in filtration rate, and accurate flow distribution between filters and banks of filters is important. Sudden changes in flowrate can lead to particle (and therefore algal) breakthrough. Filters can be less effective for solids removal, with higher turbidity and particle counts in the filtered water, for a short period after they are brought back into operation. A slow start-up, with gradually increasing filtration rate over the first hour or so, may be beneficial to minimise the effects of this. A "delayed" start, with the filter left to stand for a few minutes after backwashing, can also be beneficial in reducing the start-up peaks in turbidity and particle counts. This is known as filter "ripening".

BACKWASHING

Backwashing should provide a minimum bed expansion of 10 to 20% to ensure fluidisation and adequate cleaning of the media. The wash rate needed is governed by media size, type and water temperature. Higher rates are needed at higher temperatures because of the lower viscosity of water. Dual-media and multi-media beds need slightly greater bed expansions than single media beds to maintain a good stratification of the media. Backwash flow should be confirmed with media suppliers, and the backwash performance should be checked (visual inspection, treated water quality and headloss on restart) to establish appropriate rates for specific plants.

Higher backwash rates may be needed at the start of the wash to overcome the initial resistance of the bed. To prevent this, air scour is usually used before backwash to create pathways for even distribution of backwash flow through the bed. Air scour rates are normally between 20 and 40 m per hour. A smaller bed expansion may be acceptable if air scour is used first. The durations of air scour and backwash vary, but typically would be less than 5 minutes for air scour and 10 minutes for backwash. It is important to achieve even distribution of backwash water over the whole area of the filter.

Some filters have simultaneous air scour and backwash, using each at about half the rate that they would be used individually. Simultaneous air scour and backwash produces aggressive cleaning but has a particularly disruptive effect on both the filter media and support material, and should not be used on filters without appropriate modifications to the underdrains, filter floor and washwater outlet weirs. Final backwash without air scour should then be used at a high enough rate to ensure re-segregation of dual or multi-media beds.

The efficiency of backwash influences the performance of the filter in terms of the subsequent run length and filtrate quality, particularly during the start-up period.

PROCESS MONITORING AND CONTROL

Efficient filtration should provide a very high degree of removal of algal cells from the water (>99%), and is achieved through:

- maintenance of suitable filtration rates
- monitoring of filtrate quality and headloss
- initiation of backwash at the appropriate time, and provision of suitable backwash conditions
- maintenance of satisfactory chemical dosing conditions
- prevention or minimisation of flow surges

Good flow distribution between filters is critical. Provision of permanently installed flow measurement devices on each filter can be expensive, but temporary methods are available for checking flow distributions.

Backwash is initiated either on time of operation or headloss. Turbidity can also be used, the backwash being initiated when turbidity reaches a particular value. Suitable monitors are therefore needed on individual filters.

PERFORMANCE OPTIMISATION FOR ALGAE REMOVAL

Operational practices that can minimise the risk of algal breakthrough are reviewed below. Some of these could be implemented only at times of greater algal toxin risk, although good operating practice could best be demonstrated through routine continuous use.

1) The risk of particle breakthrough into the filtered water is greatest during the early part of the filter run, because of the higher turbidity and particle counts which occur on filter start-up, and this period should be given particular attention for reducing the risk of algal breakthrough.
2) Check turbidity from individual filters to identify any poor performers. Measure flow distribution between individual filters, if possible, to see if this could be causing poor performance.
3) Check the suitability of backwash regimes with regard to flow rates and the achievement of good dispersion of air scour (visual inspection). Measure backwash and air flow rates. Routinely check quality of backwash water leaving the beds during the wash, and headloss on restart.
4) Monitor media depths to check for long term loss of media. Overflow of water from the filter during air scour should be avoided if possible, as this can lead to loss of media. Core samples of the media can give a useful indication of media quality and grading.
5) Backwashing of individual filters should be staggered over as long a period as possible to balance out the effects of startup quality and flow rate changes to remaining filters.
6) Attempts should be made to reduce the impact of filter start-up. Possible options to achieve this are:
    - run to waste or recycle of filtrate;
    - implementation of slow start or delayed start (delay between the end of the wash cycle and restart of filtration);
    - improved backwash conditions.

These are listed in probable order of effectiveness for most works. Combinations of these may be suitable for many sites.

1) Optimisation of the slow start conditions should be investigated based on particle counting rather than turbidity. Once optimised, performance could be monitored routinely using turbidity as an indicator.
2) Sudden flow rate changes to filters should be minimised. A maximum rate of 5% per minute has been suggested.
3) Most commonly flowrate change occurs to the remaining filters in a bank when one filter is taken out of service for backwashing. Slow shut-down of filters at the end of the run can minimise the impact of this.
4) If a filter is shut down before the normal end of the run, it should be backwashed, if possible, before restart, as this reduces the frequency and magnitude of peaks in particle counts/turbidity in the filtered water. The importance of backwashing before restart increases with the length of the run before the operation is stopped.
5) At times of high algal concentrations conditions in the filter may lead to algal cell lysis and significant release of toxin. At such times, backwashing should be carried out more regularly to remove accumulated algal biomass to minimise the risk from this. It may be possible to identify a maximum acceptable headloss,

and use this as a target to initiate backwash, rather than base backwash frequency on time or turbidity breakthrough. However, under summer conditions with warm water, it is likely that filter run times in excess of 24 hours would lead to biological breakdown of algae trapped within the filter.

Return to level 1

MEMBRANE FILTRATION

MEMBRANE MODULES

Membrane plants are designed to provide as large a surface area of membrane as possible for a given size of unit. The two types of membrane modules most commonly used to achieve this are the spirally-wound and hollow fibre configurations. Spirally-wound elements consist of two layers of membrane separated by sheets of porous fabric, wrapped around a central collection pipe for the treated water. Hollow fibre elements consist of bundles of fine diameter (50 - 100 µm) tubes of membrane packed into pressure vessels. In both of these configurations the water needs to pass through narrow constrictions, and pre-filtration is needed to prevent blockage by suspended material.

Return to level 1 (cyanobacteria removal)

Return to level 1 (cyanotoxin removal)

PERMEATE FLOW RATE

One of the most important aspects of membrane process design is the water flux, measured as permeate flow divided by the membrane area ($l/m^2.h$). Typical flux rates for each of the membrane types are shown in Table 5-1(L2).

Table 5-1(L2) Typical membrane flux rates

Membrane type	Typical flux rate (l/m^2h)
Microfiltration	50 - > 100
Ultrafiltration	40 - 80
Nanofiltration	25 – 35
Reverse Osmosis	20

Reduction in flux occurs through fouling of the membrane; this can result from inorganics (e.g. calcium carbonate), particulates, natural organics or biological growth. Particulate fouling can often be overcome by backwashing, whereas other types of fouling may require chemical treatment of the membrane.

Return to level 1 (cyanobacteria removal)

Return to level 1 (cyanotoxin removal)

PRETREATMENTS

Pretreatment is usually carried out to improve membrane performance; the most common method is pre-filtration which reduces the solids loading on the membranes, and reduces backwash requirements. Other pretreatments may be applied, which improve the overall treatment process, but may not improve membrane filtration. One example is the use of PAC applied upstream of a UF or MF membrane process, to remove disinfection by-product precursors; this could also be used for cyanotoxins. Pre-chlorination may be used for some types of membrane, for example to reduce biological fouling of the membrane, although this process should be used with caution in the presence of

cyanobacteria due to possible cell lysis and toxin release. Coagulation can be used prior to UF and MF to reduce DOC concentration and reduce fouling of the membrane. The coagulant used is often alum chlorohydrate, or ferric chloride.

Return to level 1 (cyanobacteria removal)

Return to level 1 (cyanotoxin removal)

PROCESS MONITORING AND CONTROL

Membrane flux decreases during operation, and frequent backwashing is carried out to overcome this. Backwashing is usually based on time of operation (e.g. hourly for UF and MF plants), although it may be initiated on loss of flux or increasing pressure drop. Long term loss of flux is overcome by chemically enhanced backwash (CEB) or chemical clean in place (CIP), using acid, alkali, hypochlorite or proprietary cleaning products, depending on the nature of the fouling.

The integrity of membranes can deteriorate over time, such that rejection decreases i.e. more of the material that the membrane should retain passes into the treated water. UF and MF plants have integrity test procedures to identify reductions in particulate removal that may not be apparent from other measurements. These tests usually involve application of air pressure, and small perforations of the membrane are apparent from a reduction in pressure and/or presence of bubbles in the permeate side of the membrane.

Return to level 1 (cyanobacteria removal)

Return to level 1 (cyanotoxin removal)

PRESSURISED OR SUBMERGED MEMBRANES

A major factor in choice of MF and UF membrane plant is whether to install a pressurised or a submerged membrane system. The former uses hollow fibre membrane modules in tubular pressure vessels, with feed water pumps driving the water though the membrane at typically 0.5 – 1 bar pressure differential. Submerged membranes use modules in tanks, with a vacuum applied to draw water through the membrane. Operating pressure differentials are lower for immersed systems, so more modules are needed, although this may be offset by a more compact packing arrangement for the modules compared with pressure systems. Operating costs for electricity are lower than for pressurised systems, because of the lower pressure differentials. Submerged membrane plants are less mechanically complex, particularly in relation to numbers of valves, and can therefore be easier to operate.

Return to level 1 (cyanobacteria removal)

Return to level 1 (cyanotoxin removal)

DEAD-END OR CROSSFLOW

Two alternative modes of operation can be used for pressurised systems: dead-end or crossflow. The latter involves recycling of water to provide a flushing action across the membrane surface, which can reduce fouling and cleaning frequencies, particularly for feed waters with higher suspended solids. Operating costs for pumping will be higher than for dead-end operation because of the recirculation flow.

Return to level 1 *(cyanobacteria removal)*

Return to level 1 *(cyanotoxin removal)*

CYANOBACTERIAL TOXIN REMOVAL

PHYSICAL PROCESSES

ACTIVATED CARBON

MANUFACTURE

Activated carbon is formed by the conversion of carbon from primary materials such as coal, wood, peat or coconut shells. The material is converted into a highly porous structure by heating in the presence of steam, air, or sometimes chemicals to temperatures in the range of 600-1000 °C. During this process the raw material is converted to layers of 6 membered carbon rings which are bound by physical forces into groups called microcrystallites. The spaces between these microcrystallites, the pores, provide the very large surface area for adsorption. Due to the nature of the starting materials there is always some inorganic material remaining on the surface (N, Fe, S, P, Na, Cl, Si), however, by far the most abundant elements present on the surface of activated carbon are carbon (approximately 80 to 98%) and oxygen (approximately 2 to 20%). The oxygen is present mainly as carbon-oxygen surface groups such as phenolic and carboxyl groups [31]. The internal structure of activated carbon, i.e. the sizes and numbers of the pores, as well of the chemistry of the surface, will depend on the starting material and the activation processes, and will affect the adsorption of target compounds such as algal toxins [32].

Figure 5-3(L2) shows some scanning electron micrographs of two types of activated carbon. The very different external structure of the carbons is also reflected in the internal porous structure and surface chemistry.

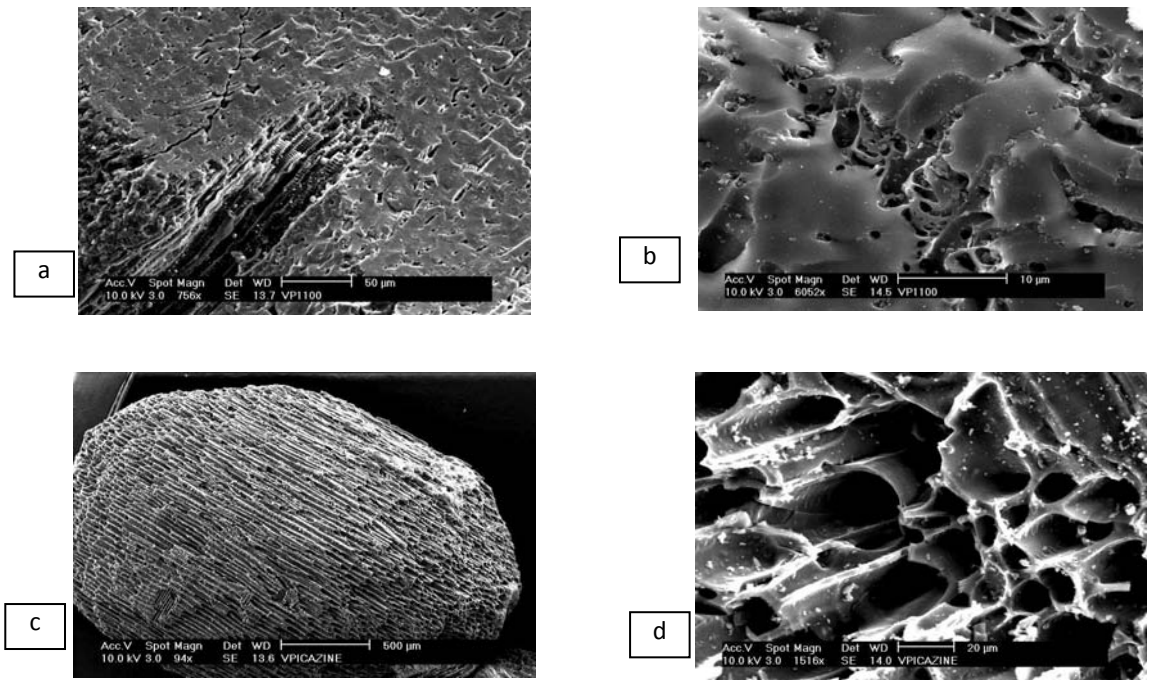

Figure 5-3(L2) Scanning electron micrographs of external activated carbon structure, a) and b) coconut-based activated carbon c) and d) wood-based, chemically activated carbon

Return to level 1

CHARACTERISATION OF ACTIVATED CARBONS

A number of tests are available for characterisation of activated carbons, and activated carbons are described in terms of these characteristics.

SURFACE AREA DETERMINATION AND PORE SIZE DISTRIBUTIONS

These parameters are usually determined using gas adsorption, most commonly nitrogen. The amount of nitrogen adsorbed is measured as a function of the relative pressure, and, based on the size of the N_2 molecule, and using one of a number of theoretical models, surface area and pore size can be calculated. The surface area can be a useful general guide for determining the overall area available for adsorption. For example, a carbon with a surface area of about 500 $m^2 g^{-1}$ would probably not be suitable for the removal of tastes and odours. However, a surface area of 1200 $m^2 g^{-1}$ (relatively high for an activated carbon) would not guarantee a high level of removal of these compounds, as the effectiveness of the adsorbent depends on the range of factors, mentioned above. The pore size distribution (PSD) will give a more reliable hint of whether the carbon will be suitable for a particular purpose, as the aim would be to have a carbon with a high volume of pores in the size range of the target molecule, as well as larger pores that will act as transport pores for the contaminant. The disadvantage of using PSDs is that the analysis is difficult, very low relative pressures of nitrogen are required, and the reproducibility between laboratories is not high.

The pores on activated carbon are categorised according to their size as follows-[33].

Primary micro pores	< 0.8 nanometre (nm)
Secondary micro pores	0.8 - nm - 2 nm
Mesopores	2 nm -50 nm
Macropores	> 50 nm

(One nanometre is one millionth of a millimetre.)

IODINE NUMBER

The iodine number is obtained from a series of adsorption experiments measuring the amount of iodine removed from solution by activated carbon. As iodine is a relatively small molecule it is assumed that the iodine number is an indication of the number of micropores, or the surface area. A value of 800 or higher suggests a high surface area, high “activity” carbon [34].

MOLASSES NUMBER

For this test a solution of backstrap molasses is prepared, and the activated carbon is added. The removal of colour in the solution is measured using UV spectroscopy. Molasses is the syrup remaining after processing sugar cane or sugar beet to obtain sugar. Backstrap molasses is the darkest of the by-products, and contains an unknown mixture of large organic molecules, some of which are highly coloured. It is assumed that the more colour adsorbed by the carbon, the more effective it will be for the adsorption of large organic compounds from water. In reality the number may reflect the volume of large pores, perhaps mesopores, in the carbon structure. A reasonable value for activated carbon is around 250.

TANNIN NUMBER

The tannin number is defined as the concentration of carbon, in mg L^{-1} required to reduce a standard tannin solution from a concentration of 20 to 2 mg L^{-1}. The standard Merck tannic acid recommended for use in this test has a molecular weight of approximately 1700 g mol^{-1}. The tannin number can give an indication of the adsorption capacity of the carbon for DOC, and the lower the tannin number the better the adsorption of tannin.

Essentially the four methods above give good general information, but give specific removal information only about the compound used in the test (e.g. iodine, tannin). Details of the three tests undertaken in aqueous solution are given in the American Water Works Association Standards list, published in 2002.

DENSITY

This parameter is often quoted by manufacturers. In general, a carbon with low density has a large volume of larger pores, such as macropores and mesopores, and relatively fewer micropores. It is also more likely to float, or be abraded during backwashing, which may be an issue for GAC.

ABRASION RESISTANCE

This number gives an indication of the "robustness" of an activated carbon particle. Of particular importance with GAC, where losses can be high through abrasion of particles during frequent backwashing.

PARTICLE SIZE

For GAC filtration, the particle size required will be determined by the physical requirements for effective filtration at the flow rates experienced in the plant, as well as the mode of backwashing utilised. The particle size of PAC is a major influence on the rate of removal of target compounds; the smaller the particle, the higher the rate of removal. As a result, shorter contact times and lower doses are required for smaller PAC particles. However, the advantages are somewhat overcome by the difficulties of removing and handling very small particles of black powder. A diameter of approximately 11 micron has been found to result in high rates of adsorption without major difficulties in removal and handling.

The interpretation of the data obtained using the tests listed above is not trivial, and any perceived relationship between the iodine number and, for example, the amount of cylindrospermopsin adsorbed in 30 mins, is tenuous at best. Although this information is useful, and many of these parameters can be supplied by the activated carbon manufacturer, it is very difficult to use them to help decide on a brand, or raw material for the removal of a particular compound (except, of course, if the target compound is iodine, tannin, or molasses). However, some generalisations can be made regarding the choice of activated carbon for the removal of algal toxins.

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THE ADSORPTION PROCESS

Removal of contaminants by activated carbon is a complex process. Figure 5-4(L2) is a schematic representation of the major processes occurring during adsorption, these are largely diffusion related. In order to be removed by activated carbon a molecule must diffuse:

-to the particle surface from the bulk liquid (1)

-through the liquid surface layer (2)

-through the pore structure of the carbon (3)

finally being removed from solution at the adsorption site (4) (see Figure 5-4(L2))

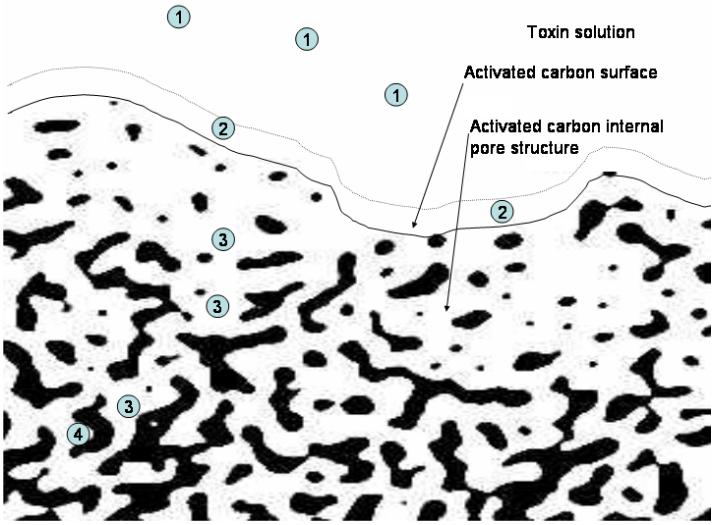

Figure 5-4(L2) Representation of diffusion into the activated carbon structure

Processes 1 and 2 depend on the physical parameters of the system, for example mixing conditions for PAC, flow rates for GAC. Processes 3 and 4 are dependent on the activated carbon pore size distribution and surface chemistry/hydrophobicity. In general, the most favourable energy for adsorption is provided by pores slightly larger than the adsorbing molecule, as there are more contact points for the compound to adhere, and it fits “snugly” into the pore. In water treatment another very important factor is how quickly the contaminant can reach a suitable adsorption site. This is strongly influenced by the access to the internal structure through the pores on the external surface, as well as the structure and size of the “transport pores”, those the contaminant must travel prior to reaching the adsorption site (i.e. step 3,Figure 5-4(L2)).

Physical adsorption is the primary means by which activated carbon works to remove contaminants from water. The highly porous structure provides a large surface area for contaminants (adsorbates) to collect. Physical adsorption occurs because all molecules exert attractive forces, especially molecules at the surface of a solid. The large internal surface area of carbon has many attractive forces which work to attract other molecules. One of the main forces is the attraction between the hydrophobic (“water fearing”) carbon surface and a hydrophobic molecule, or one with hydrophobic parts. The oxygen functional groups impart polarity and, if they dissociate, a charge to the surface, thus they allow adsorption through hydrogen bonding or electrostatic attraction [35].

Due to its very effective porous nature activated carbon adsorbs most compounds present in water to some extent. Although carbon has a very high surface area, invariably there are limited suitable adsorption sites available. A competition is set up between the different species for those adsorption sites, and adsorption of the compound of interest will usually be reduced [36]. The main competing species in surface water are those compounds formed by the breakdown of vegetable and animal matter in the environment, dissolved natural organic material (NOM). This mixture of compounds is collectively measured by dissolved organic carbon (DOC) analysis, or ultraviolet (UV) absorbance measurements.

The factors that influence the adsorption of contaminants, such as pore size distribution and surface characteristics, are dependent on the starting material and method of activation. Even small variations in the chemical composition of

the raw material and activation conditions can result in large differences in the finished product. A range of tests is available to characterise activated carbons with the aim of determining the most appropriate adsorbent for a particular contaminant. Broadly speaking these recommendations apply to both PAC and GAC. Both overall capacity and adsorption rates are also important for GAC filtration. As for PAC, a comparative test is recommended. Details of a useful comparative test for GAC are given below.

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POWDERED ACTIVATED CARBON

PAC PROCESS DESIGN

Flow conditions in the pipework carrying PAC dosed water, should be maintained at sufficient flow/velocity to avoid settlement of PAC and achieve good mixing. PAC particle size is typically in the range 40-80 µm and apparent (bulk) density in the range 360-740 kg/m^3 (assuming a voidage of 0.4, true density would be in the range 600 - 1233 kg per m^3). A particle of 80 µm diameter and density 1233 kg per m^3 would settle at a rate of about 3 cm min^{-1}. The particles should be maintained in suspension by maintaining turbulent flow conditions in the raw water main. Table 5-2(L2) shows minimum velocities and flows to maintain turbulent conditions in a range of pipe sizes.

Table 5-2(L2) Velocity and flow required to maintain turbulent conditions

Pipe diameter (mm)	Velocity required (m/s)	Flow required (m^3/h)
100	0.05	1.3
200	0.02	2.6
300	0.02	3.9
500	0.01	6.4
1000	0.005	12.9

Calculations assume a water temperature of 5 °C, smooth pipes and a Reynold's number of 3000.

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COMPARATIVE TEST FOR PAC

This test can be applied to determine the most cost-effective PAC for application in a water treatment plant.

1. Choose 3-6 good quality activated carbons with the general attributes required for the toxin of interest (see main text). The manufacturer will give general guidance regarding raw materials and average pore sizes.
2. Sample water from the position in the plant where the PAC will be applied. Spike the water with the concentration of toxin that might be expected at the application point. If this is unknown, 5 µg L^{-1} of toxin (for saxitoxins STX equivalents) is a value that will give representative results if converted to percent removals. Take a sample for toxin analysis.
3. Place 500 mL of spiked water into each of three jar testing vessels
4. Add 5, 10, and 30 mg L^{-1} of PAC* into the separate jar test vessels, with stirring.

5 Continue stirring for the average contact time expected after the point of application in the plant. This could be the middle of the range expected over the period of possible toxin contamination. Assume the effective contact time is only while the particles are in suspension in the plant. Disregard time during settling when determining contact time.

6 After the appropriate contact time, filter sample through membrane filter (0.45 μm), analyse samples for toxin concentration, or send to appropriate laboratory.

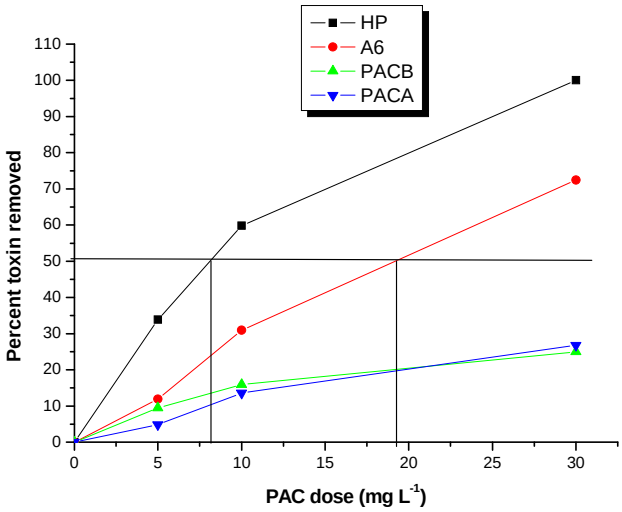
7 Undertake this test for each PAC.

8 Estimate the PAC dose required for 50% removal of the toxin. This can be determined approximately by interpolating a graph of percent removal vs carbon dose (see Figure 5-5(L2)).

9 Multiply the cost per kilogram of the carbon by the dose required, and a simple cost analysis of the carbons can be achieved.

* Prepare a slurry for each carbon by adding 50 mg to 50 cm^3 of milli-Q water or 1:1, one day before running the test

An example of this procedure for microcystins-LR for four carbons is shown in the graph and table in Figure 5-5(L2).



PAC	Dose required for 50% removal	Cost per kilogram	Cost per ML of water treated
1	8	4.20	**$34**
2	19	1.80	**$35**
3	>>30	3.80	**>>$ 114**
4	>>30	2.30	**>> $69**

Figure 5-5(L2) An example of a comparative test for PAC and cost analysis

In this example the most expensive carbon is the most cost effective for the removal of this contaminant.

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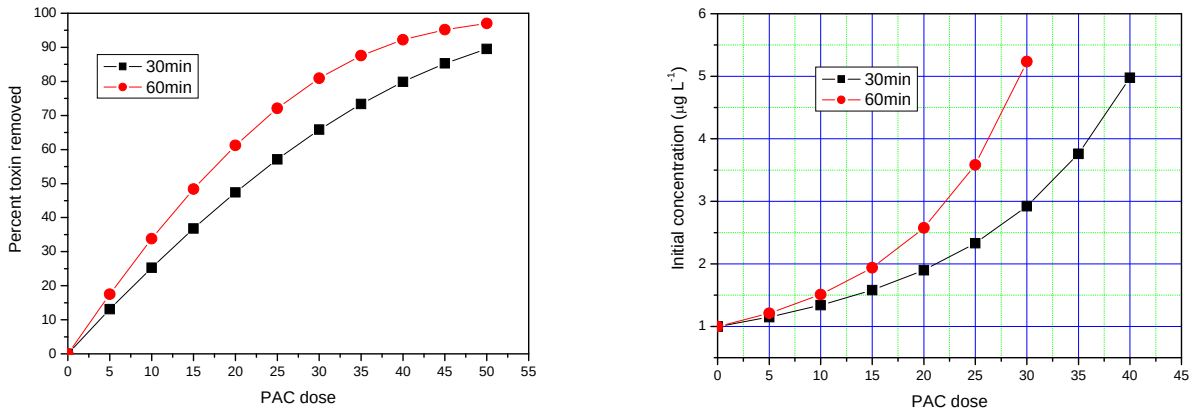
CONSTRUCTION OF PAC DOSE REQUIREMENT CURVES

This method is simply an extension of the comparative test described in the section above. Once the most cost-effective activated carbon has been chosen a series of jar tests should be carried out over a larger range of doses, to obtain percent removals from 20 to 90%. These results can be applied to any concentration of toxin as the percent removal is independent of the initial concentration. At least 5 carbon doses should be used to obtain an accurate removal vs dose curve. This should be undertaken at two contact times if the plant could experience a variation in flow affecting the contact time for the PAC. An example is given in Figure 5-6(L2)a) below. To improve the ease of use of this graph, percent removal could be converted to initial concentration. If we assume a target concentration of 1 µg L^{-1} of toxin, the y axis data can be converted to initial concentration using the equation:

Initial concentration =100/(100-percent removal)
For example, 50% removal on the graph would apply to 100/(100-50)=100/50=2 µg L^{-1}
In other words, if the aim is to reduce the concentration of toxin from 2 µg L^{-1} to 1 µg L^{-1} the removal we need is 50%.

Figure 5-6(L2)b shows the same data as Figure 5-6(L2)a, with the percent removal axis converted to initial concentration. Both graphs are equally valid, although b) might be preferred for simplicity.



a b

Figure 5-6(L2) Indicative PAC dose required for percent toxin removal (a) and to achieve a final concentration of 1 µg L^{-1} (b)

It is relatively easy to determine from Figure 5-6(L2)b that an inlet concentration of 2 µg L^{-1} will require a PAC dose of 15 mg L^{-1} with a contact time of 60 minutes, and 20 mg L^{-1} for a contact time of 30 minutes.

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GRANULAR ACTIVATED CARBON

PROCESS MONITORING AND CONTROL

When the contaminant driving the renewing of the GAC is present in the feedwater continuously, routine sampling of treated water from individual beds is the most common way of identifying breakthrough and the need for regeneration. Whilst this can provide a primarily reactive tool for ensuring that excessive breakthrough does not occur, and can monitor the suitability of an existing regeneration strategy, alone it does not allow any long term planning of regeneration schedules.

The most secure and practical schedule for regeneration (or the replacement of the GAC in the absence of regeneration facilities) involves “staggering”, with beds at different levels of exhaustion and regeneration of the longest running bed at fixed intervals. This offers the following advantages:

- the majority of the beds will have spare capacity to protect against shock loads
- GAC handling is spread over an extended period, rather than the whole works inventory needing to be regenerated over a short time
- each bed in turn can be operated to a predetermined breakthrough concentration above the concentration goal, because of dilution by water from the other beds, which increases the overall adsorption capacity of the system. The potential for this will depend upon the degree of security required, the sampling frequency and delay in obtaining the results, and the time taken to arrange regeneration and replace the GAC

The disadvantages of this mode of operation lie in the need to protect against breakthrough from the longest running bed, and to establish the stagger initially. This means either that new adsorbers have to be brought into service at intervals (probably not practical for most works) or some beds have to be regenerated early, thus losing some potential capacity during the first few years of operation.

For the simplest case, the stagger can be established by estimating the maximum bed life to a treatment target breakthrough concentration, and dividing this by the number of beds to identify the interval between regenerations. If breakthrough curves are available (e.g. from pilot plant trials), these can be used to refine the treatment target concentration from a single bed, using an iterative approach. From the breakthrough curve, the bed life to a treatment target is derived, and this bed life is divided equally by the number of adsorbers to identify the interval between regenerations. The concentration from each bed at this point, and therefore in the final water (i.e. mixed water from all beds), can be identified from the breakthrough curve. The concentration in the final water can be compared with the required quality standard. The treatment target can then be modified upwards or downwards, and the procedure repeated until the required margin of security is achieved (i.e. the minimum acceptable difference between quality standard leaving the works and the calculated mean from this approach). This is illustrated in Figure 5-7(L2). However, for seasonal contaminants such as toxins there will be a need to modify this approach to target higher risk periods, which is considered below.

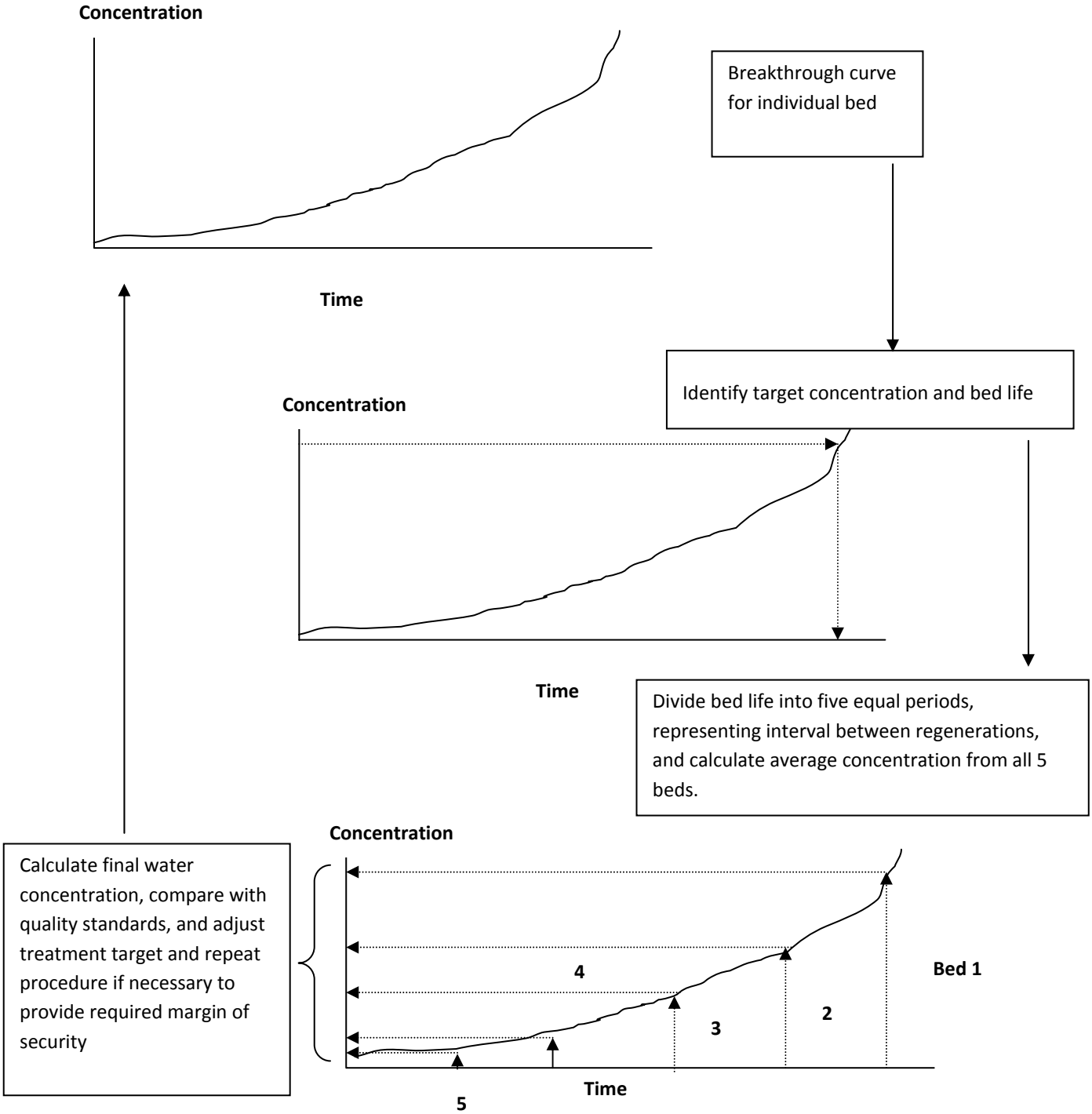

Figure 5-7(L2) Illustration of iterative approach to establishing regeneration schedule for plant with 5 adsorbers

REGENERATION SCHEDULE FOR SEASONAL CONTAMINANTS

Regeneration schedules should make allowance for any seasonal effects, for contaminants such as cyanotoxins. The stagger should be established to take this seasonality into account, to ensure that more beds have been recently

regenerated shortly before the cyanotoxin load is expected. Checks can also be made to evaluate whether shock loads can be dealt with, particularly by the longest running beds. A suggested operational approach for is as follows:

1) Take core samples at intervals, particularly before seasonal contamination might be expected, from the longest running bed and from the bed that has been in operation for the shortest time. Another bed could be included with intermediate run time between these two.

2) Take a representative sample from different depths within each bed (at least from the top half and bottom half).

3) Carry out adsorption isotherm tests on each sample, using appropriate water spiked with the relevant contaminants. Or use the *simplified GAC monitoring test*

Whilst this may not provide an accurate quantification of remaining capacity, it should allow an assessment to be made of the capability of the longer running beds to deal with a sudden increase in load. The most significant feature to identify would be the capacity of the lower part of the oldest bed compared with the upper parts of the bed, and with other beds.

Procedures should be in place to monitor the suitability of the regeneration schedule. As a minimum, this should involve routine sampling of treated water from individual adsorbers, with particular attention being given to the longest running beds. A more rigorous approach may be needed at some sites, particularly with widely varying concentrations of contaminants (e.g. due to algal growth), involving the estimation of loading and remaining capacity for specific contaminants.

The effectiveness of regeneration should be assessed and documented, using at least one procedure in each of the following categories:

- Adsorption properties before and after regeneration e.g. iodine number, methylene blue number.
- Chemical properties: e.g. ash content, leachables.
- Physical properties: e.g. apparent density, particle size range, attrition test.
- Loss of weight and volume on regeneration should also be obtained.

Consistency with relevant standards should be confirmed for regenerated GAC, and procedures should be in place to protect treated water quality on restart with freshly regenerated GAC. It may be necessary to operate a regenerated absorber to waste, until water quality (particularly pH) stabilises.

Monitoring of the feed water and flowrate can allow calculation of the approximate GAC loading at any point in time, and, based on historical data, an estimate of the remaining capacity. This may be adequate for situations where the raw water quality is relatively constant, and where data are available for estimating capacity.

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COMPARATIVE TEST FOR GAC

Testing to determine the most effective GAC in the laboratory is not as straightforward as PAC. Under normal conditions (i.e. 6-20 minute contact time) most virgin GAC will adsorb organic contaminants to below detection, perhaps for a prolonged period. It is therefore very difficult to compare several GACs. Long term pilot plant studies are recommended to determine the most effective GAC and the approximate time until breakthrough of the contaminant. However, these tests are difficult, expensive and time consuming. A simple alternative to determine the most

effective GAC is the short-bed adsorber test in combination with an equilibrium isotherm test. Equilibrium isotherms can be used to compare the capacities of the GACs for the contaminant, and short bed adsorber tests give an indication of the rates of adsorption. Two sets of experiments are required.

Equilibrium isotherms:

1 Sample water at the point in the treatment plant where the GAC will be situated, spike in toxin at a concentration of approximately 5 µg L^{-1}.

2 Place equal volumes of spiked water in each of 5 glass vessels. Volumes of 250-500 mL are preferred.

3 Add GAC, ground to < 45 µm, to 4 of the vessels at doses of 2, 6, 10 15 mg L^{-1}. The 6th vessel will act as the control.

4 Mix vessels consistently to maintain activated carbon in suspension for 3 days.

5 Filter all samples and analyse for toxins.

6 Undertake his test for each carbon and plot percent removed vs carbon dose for each carbon (see Figure 5-8(L2)a).

Short bed column tests:

These tests are designed to force breakthrough of the contaminant for the comparison of different carbons

1 Pack GAC into small diameter column (1 cm) to a bed depth of 4 cm.

2 Pump toxin spiked test water through column at a flow rate equivalent to the filtration rate expected on the filters

3 Collect column outlet samples at regular intervals for a period of 2 hours

4 Analyse samples for toxins and plot percent toxin breakthrough vs time (Figure 5-8(L2)b)

A GAC that shows superior equilibrium capacity and removal in the short bed adsorber test could be expected to perform best at the full scale. In the example below, GACs 1 and 3 appear equivalent and the decision would depend on relative costs

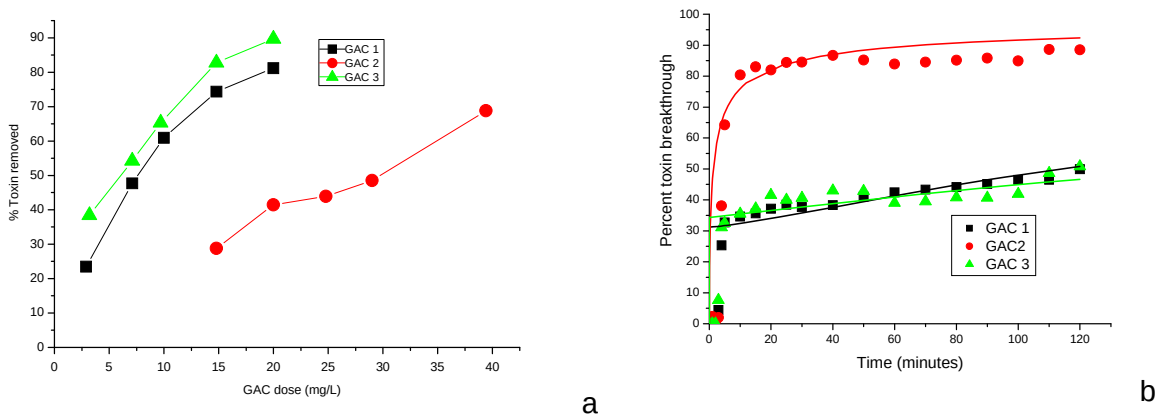

Figure 5-8(L2) Comparative test for GAC. Adsorption isotherms (a) and short bed column test (b)

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GENERAL GUIDANCE FOR GAC SELECTION

It is necessary to identify the most effective GAC for a particular situation, depending on the water type, application and contaminants to be removed. Reliable choice of the most cost effective GAC needs to be based at least on laboratory tests, and ideally on pilot plant trials. Table 5-3(L2) provides general guidance on GAC selection.

Table 5-3(L2) General guidance on selection of GAC

Application	Considerations for GAC selection
Removal of cyanotoxins from surface water, using post filter gravity adsorber	Smaller grain size (e.g. effective size 0.7 mm) and higher uniformity coefficient (e.g. 1.7 – 1.9). If headloss limitations, greater effective size (e.g. 0.9 mm) may be desirable to reduce backwash frequency. Higher overall capacity to deal with background organics (i.e. Iodine Number >1000 mg g^{-1}, Methylene Blue Number >240 mg g^{-1}).
Removal of cyanotoxins from surface water, using GAC as first stage filter media	Need GAC suitable for filtration applications, with larger grain size (e.g. effective size 1 mm) and lower uniformity coefficient (e.g. < 1.5). Higher overall capacity to deal with background organics (i.e. Iodine Number >1000 mg/g, Methylene Blue Number >240 mg g^{-1}). Lower values may be suitable for low TOC feed water (e.g. <2mg L^{-1}).

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EMPTY BED CONTACT TIME

The service life of the bed is dependent on the capacity of the carbon used and the empty bed contact time (EBCT):

$$\text{EBCT} = \frac{\text{Volume of GAC } (m^3)}{\text{Water flowrate } (m^3 / \text{minute})} \text{ (minutes)}$$

Or alternatively

$$\text{EBCT} = \frac{\text{depth of bed (m) x 60}}{\text{filtration rate (m / hour)}} \text{ (minutes)}$$

EBCTs are usually in the range 5 to 20 minutes, depending on the application. Doubling the EBCT will roughly double the service life, possibly giving some reduction in regeneration costs per unit volume treated (depending on the amount of carbon used), at the expense of higher capital cost.

By selecting suitable EBCT and GAC, a long service life (one year or more) can be obtained for many applications. For mixtures of organic compounds, the service life can be governed by the compound which breaks through first. GACs vary considerably in their capacity for specific organic compounds, which can have a considerable effect on service life. A guide to capacity can be obtained from batch equilibrium isotherm tests, but it is difficult to predict bed performance from such tests. Rapid column tests and mathematical models have been developed to help select the best GAC for a particular application, and provide a better prediction of bed life.

A parameter often used to compare GAC performance is the effective carbon dose (ECD) defined as:

$$ECD = \frac{\text{Weight of GAC in bed (g)}}{\text{Volume of water treated during service run } (m^3)}$$

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GAC MONITORING TEST

When GAC has been in use for 6 months or more it is worthwhile to begin to monitor for removal efficiency. For example, if a bloom of *Microcystis* were possible as the warmer months approach, a simple test for microcystin removal will give an indication of the GAC filter's ability to remove the toxin effectively.

Laboratory scale filter columns can be used for this test. A column diameter of 2.5 cm and a bed depth of 7-8 cm has been shown to be optimum. Larger pilot columns can also be used; in this case large volumes of water containing toxin will be required. This may prove an expensive exercise if the test is undertaken using commercial toxin standards.

The test can be conducted as follows

1. Take duplicate samples of 100 mL from the top of each GAC filter after backwash.
2. Place in glass column, 2.5 cm diameter, to a bed depth of 7-8 cm.
3. Pump water, sampled from the plant prior to the GAC filters and spiked with toxin, at a flow rate to achieve the same empty bed contact time as the full scale GAC filters.
4. After several hours take samples from the inlet to the column, and the outlet.
5. Repeat for other GAC samples
6. Analyse samples for toxin and calculate average percent removal.

Clearly this is not a definitive test to determine full scale removals as the samples will not necessarily be representative of the whole filter. However, it can be used to give an *indication* of how the GAC filters would perform. For example, if the small scale column showed an average of 50% removal of microcystin, and this is the level of removal that would be necessary in the plant, it would be wise to consider replacement of the GAC.

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CHEMICAL PROCESSES

OZONATION

PROCESS DESCRIPTION

The main features of an ozonation plant (Figure 5-9(L2)) are described below:

- Feed gas drying equipment: dry air or oxygen is needed to minimise power consumption by the ozoniser. The gas is dried by cooling to cause condensation, followed by adsorption of moisture.

- Ozone generator, usually of the tube type with concentric electrodes in glass tubes surrounded by cooling water.
- Contact tank in which the water is dosed with the ozone-enriched air by means of diffusers at the base. Water depth is typically 5 m deep, providing 10 to 20 minutes contact time in baffled tanks. Some designs allow for recycle and re-injection of this gas to increase the ozonation efficiency. However, these are not in common use.
- Ozone destructor to treat the off-gas from the contactor. The ozone is normally broken down catalytically using metal oxide catalysts, but some designs use an electric furnace heated to 300°C.

Care must be taken in selecting suitable materials for construction of the contactor and, more importantly, the pipework carrying ozonated air. Installation of ozonation plant in existing treatment works may involve considerable engineering complexity compared with the requirements for other chemicals or oxidants.

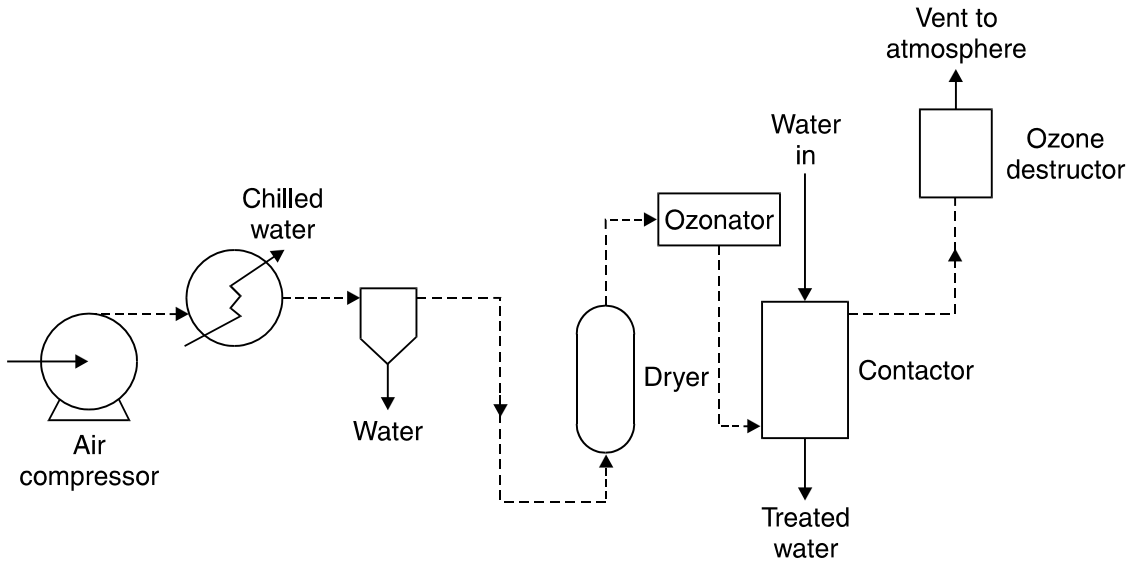

Figure 5-9(L2) Main features of an ozonation plant, ozone generation from air

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POTASSIUM PERMANGANATE

PROCESS DESCRIPTION

Potassium permanganate is normally supplied as a granular powder, and is dosed as a solution, typically at around 10 mg L^{-1}. It reacts with both organic and inorganic constituents in the water, but is most commonly used as a pre-treatment for oxidation of iron and manganese in raw water. The oxidant converts dissolved manganese into insoluble manganese oxides, which can be removed by filtration.

The dose rate is usually set manually, with automatic flow proportional control of pump speed. Although dedicated online monitors for potassium permanganate are not available, it would be possible to measure concentration by calibration of a spectrophotometer, measuring adsorption at 550 nm. Typically, the permanganate dose is adjusted to slightly less than the stoichiometric 'demand' for oxidation of manganese or iron, to avoid problems with pink coloration of the final water. The dose requirement will vary with pH and water temperature, and so requires some careful monitoring.

REMOVAL OF EXTRACELLULAR TOXINS

Doses of potassium permanganate in the range 2 to 10 mg L^{-1}, to a raw water with 2 h contact time, achieved a maximum of 48% removal of m-LR (initial concentration 4.6 µg L^{-1}). There was no residual oxidant at the end of the tests, which indicates that oxidant was probably consumed by competing natural organic matter, probably limiting removal of M-LR. A dose of 2 mg L^{-1} into treated water reduced the initial concentration of m-LR (4.0 µg L^{-1}) to below the limit of detection (0.9 µg L^{-1}). The tests were repeated for another water of different quality; 1 mg L^{-1}achieved 96% removal with raw water, and > 97% removal in treated water. Further tests with clarified and clarified/filtered water, under similar conditions, showed no difference between the two water types[5]. A dose of 0.7 mg L^{-1}achieved 76% removal of m-LR, and 1 mg L^{-1} achieved 88% removal, for initial concentrations of between 5 and 7.2 µg L^{-1}. Removal of anatoxin-a was also found to be effective, 0.5 mg L^{-1} achieving at least 85% reduction from an initial concentration of 4.3 µg L^{-1}, and 1 mg L^{-1} achieving greater than 93% removal. In another study[4], a dose of 1 mg L^{-1} potassium permanganate had no effect on intracellular cyanotoxin, whereas doses of 2 to 3 mg L^{-1} resulted in release of intracellular cyanotoxin and removal of extracellular cyanotoxin, such that the total concentration of M-LR was reduced from 1.4 µg L^{-1} to below the limit of detection (0.6 µg L^{-1}).

Example results of simulation modelling using potassium permanganate for microcystin-LR degradation are shown in Table 5-4(L2).

Table 5-4(L2) Results of simulation modelling of oxidation of microcystin LR using potassium permanganate

Oxidant	Temp (°C)	Concentration (mg L^{-1})	Time for 90% removal of Microcystin-LR
Potassium permanganate	10	1 2	35 minutes 18 minutes
	20	1 2	23 minutes 12 minutes

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UV/PEROXIDE

Pilot plant trials of UV irradiation for destruction of microcystin-LR and anatoxin-a, with and without hydrogen peroxide, were carried out by Anglian Water in the UK using ultrafiltration treated reservoir water spiked with 1µg/l microcystin LR and 0.2 µg/l anatoxin-a. UV doses of 1000 mJ/cm^2 gave around 50% removal of both cyanotoxins. Dosing of hydrogen peroxide at >7 mg L^{-1} had a beneficial effect for removal of anatoxin by UV, but not for microcystin.

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OXIDATION REACTION RATES

One objective the EU project "TOXIC" was to develop a database of cyanotoxin degradation by oxidation laboratory trials. A summary of the results for the oxidants used in water treatment is given in Table 5-5(L2) showing reaction rate constants ($M^{-1}s^{-1}$) and half-life of the cyanotoxins at 20°C and pH 7, based on an oxidant concentration of 1 mg L^{-1}.

Table 5-5(L2) Reaction rate constants for various oxidants and toxins. From [26]

Oxidant	Microcystin-LR	Anatoxin A	Cylindrospermopsin
Chlorine dioxide	1.1 (12 h)	"Low"	0.9 (>14 h)
Permanganate	348 (5 min)	"High"	0.3 (6 d)
Ozone	4×10^5 (0.1 s)	4×10^4 (1 s)	5×10^4 (0.7 s)
HOCl	90 (10 min)	<1 (>15 h)	1100 (48 s)
Monochloramine	0.012 (30 d)	< 1 (>14 h)	<1 (>14 h)

These results indicate the relative performance of the oxidants, and the simulation models, given below, can be used to predict performance in more detail.

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MODELLING OF OXIDATION PROCESSES

APPROACH

Treatment simulation models were developed as part of the EU "TOXIC" project, and the oxidation models have been used here to provide estimated performance information for chlorine, chlorine dioxide, chloramine, potassium permanganate and ozone for microcystin-LR degradation.

Reaction between microcystins and oxidants can be expressed by second order rate constants, and kinetic data have been derived for a range of appropriate oxidants. A modelling approach has been applied, using these rate constants, to develop simple relationships between oxidant concentration, contact time and cyanotoxin breakdown for all oxidants apart from ozone. Results are provided to allow the performance of the oxidants to be evaluated for design or operational purposes.

Interpretation of the modelling data needs to take into account the hydraulics of the contact system in relation to mixing and short-circuiting, and the actual oxidant concentrations which would occur in practice. Information given below on contact tank hydraulics can be used in conjunction with the process simulation model for oxidation available as an output from the TOXIC project.

The performance of a flow-through reactor, such as an oxidant contact tank, is influenced by the hydraulics. It is convenient to consider hydraulics in terms of two extreme types of reactor:

- Plug flow reactor (PFR), in which there is no axial mixing; and
- Continuous stirred tank reactor (CSTR), in which at any moment in time the concentration of any reactant at every point in the reactor and at the outlet is equal.

The CSTR therefore represents a perfectly stirred vessel. All things being equal, a reaction will proceed further in a PFR than in a CSTR, because in a CSTR the incoming reactants are being immediately diluted. Because there is no axial mixing in a PFR every element of fluid resides in the reactor for the same time, equal to the hydraulic residence time (HRT, reactor volume divided by the flow rate). Where there is axial mixing, the residence time of some fluid in the reactor in shorter than the HRT, and for some fluid is longer than the HRT. It is for these reasons that disinfection contact tanks are designed to promote plug flow.

A pipe reactor in which fully turbulent flow is maintained can approach PFR characteristics. The hydraulics of tanks will fall somewhere between the two extremes. A common approach to describing non-ideal hydraulics is to consider a tank as a series of n CSTRs of equal volume (V/n, where V is the tank volume). The effect of increasing n can be illustrated by considering what happens when an inert tracer is instantaneously injected into the inlet of the tank, and monitored at the outlet, Figure 5-10(L2).

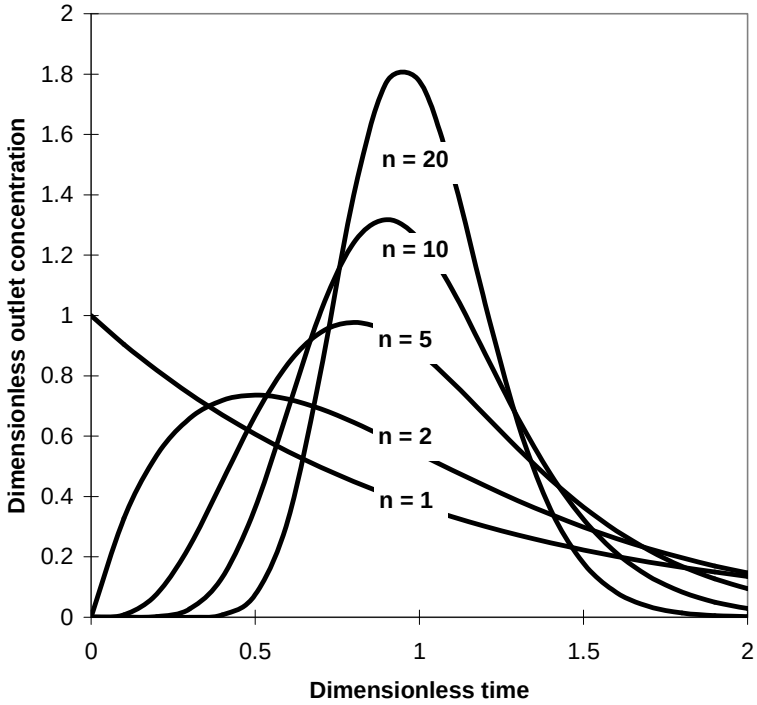

Figure 5-10(L2) Effect of number of CSTRs, n, on a tracer added instantaneously to the inlet of a tank. Note: dimensionless time = 1 is equivalent to the HRT of the tank

It can be seen in Figure 5-10(L2) that when n = 1, which represents the perfectly mixed case, the tracer is instantly dispersed throughout the tank, and the concentration then steadily declines as it is progressively diluted by incoming fluid. In a PFR all of the tracer added at time 0 would exit the tank at a time equal to the HRT, equivalent to 1 on the dimensionless time scale. As n increases, the pattern of tracer at the tank outlet approaches the PFR case. So as $n \rightarrow \infty$, the hydraulics tend to plug flow.

Procedures for carrying out tracer tests and deriving the number of CSTRs for an existing plant are given in the following section. However, modelled results are provided for three categories of hydraulic characteristics, which should adequately approximate the range of conditions found in practice:

- n = 3, which represents a moderately well mixed tank, which in practice means a tank in which little effort has been made to avoid mixing. Since in practice a tank actually designed for mixing is unlikely to achieve n < 2, n = 3 is probably the worst case
- n = 6, which represents a tank in which steps have been taken to avoid mixing, by design of the inlet and outlet and/or inclusion of baffles. A well-designed contact tank is unlikely to achieve a value of n much greater than 6; and the improvement in performance from n = 6 to, say, n = 9 is much less than from n = 3 to n = 6
- Plug flow. Plug flow can be approached in a pipe in which fully turbulent flow is maintained

The modelling approach used here assumes a constant oxidant concentration; in reality this will not occur because of oxidant decay in natural waters, but the results serve to illustrate the relative performance of the oxidants. Three approaches can be used in interpreting the results:

- the concentration can be estimated from the area under the oxidant decay curve
- an average oxidant concentration can be derived from the arithmetic mean of the dose and residual concentration
- the residual can be used to provide a conservative estimate of concentration and toxin breakdown

The first of these is the most accurate, but it is unlikely that this could be derived in practical situations, so an approximation will be needed from one of the other two approaches. Table 5-6(L2) compares chlorine concentrations from these three approaches, based on a chlorine dose of 2 mg L^{-1}, a residual of 1 mg L^{-1}, 45 minutes contact time at 20°C, and first or second order chlorine decay with suitable rate constants.

Table 5-6(L2) Comparison of chlorine concentrations (mg L^{-1}) derived from the decay curve, arithmetic mean and residual

Hydraulic characteristics	1st order decay	2nd order decay	Arithmetic mean	Residual
n = 3 CSTRs	1.28	1.24	1.5	1
n = 6 CSTRs	1.36	1.31	1.5	1
Plug flow	1.43	1.37	1.5	1

The arithmetic mean overestimates actual values based on the decay curve, and would therefore overestimate the breakdown of toxin, whereas the residual would underestimate toxin breakdown. However, the differences are not large, as illustrated in Table 5-7(L2) using modelled data for m-LR removal with chlorine. This assumes first order chlorine decay, a second order rate constant for m-LR breakdown of 72 $M^{1}.s^{-1}$, and chlorination conditions as above.

Table 5-7(L2) Comparison of M-LR removal using decay curve, arithmetic mean and residual chlorine concentrations

Hydraulic characteristics	% removal using residual (1 mg L^{-1})	% removal using decay curve	% removal using arithmetic mean (1.5 mg L^{-1})
n = 3 CSTRs	85	90 (1.28 mg L^{-1})	92
n = 6 CSTRs	89	94 (1.36 mg L^{-1})	96
Plug flow	93	>95 (1.43 mg L^{-1})	>95

PERFORMANCE

Graphical information is provided below for chlorine and permanganate to allow toxin breakdown to be estimated for existing or proposed plant, after first identifying appropriate hydraulic characteristics and oxidant concentrations as described above. The approach assumes a constant oxidant concentration to illustrate relative performance of each oxidant. Rate constants used are consistent with those given in Table 5-5(L2). Results are given in Figures 5-10(L2) to 5-13(L2).

Less detailed information on chlorine dioxide and chloramine is also provided, mainly to indicate that these are largely ineffective for toxin degradation under practical conditions.

Results for chlorine dioxide are given in Figure 5-15(L2). Under plug flow conditions chlorine dioxide concentrations of 1 mg L^{-1} and 2 mg L^{-1} would require 1 day and 0.5 days respectively to achieve 80% removal at 20°C. A very high concentration of 5 mg L^{-1} would require 7 hours contact time to achieve 90% removal.

Modelling of m-LR breakdown indicates that under plug flow conditions monochloramine concentrations of 1 mg L^{-1} and 2 mg L^{-1} would require more than 35 days and 15 days respectively to achieve 50% removal. A very high concentration of 5 mg L^{-1} would require more than 7 days contact time to achieve 50% removal and over 20 days to achieve 90% removal. Different hydraulic conditions or lower temperature would give less effective removal.

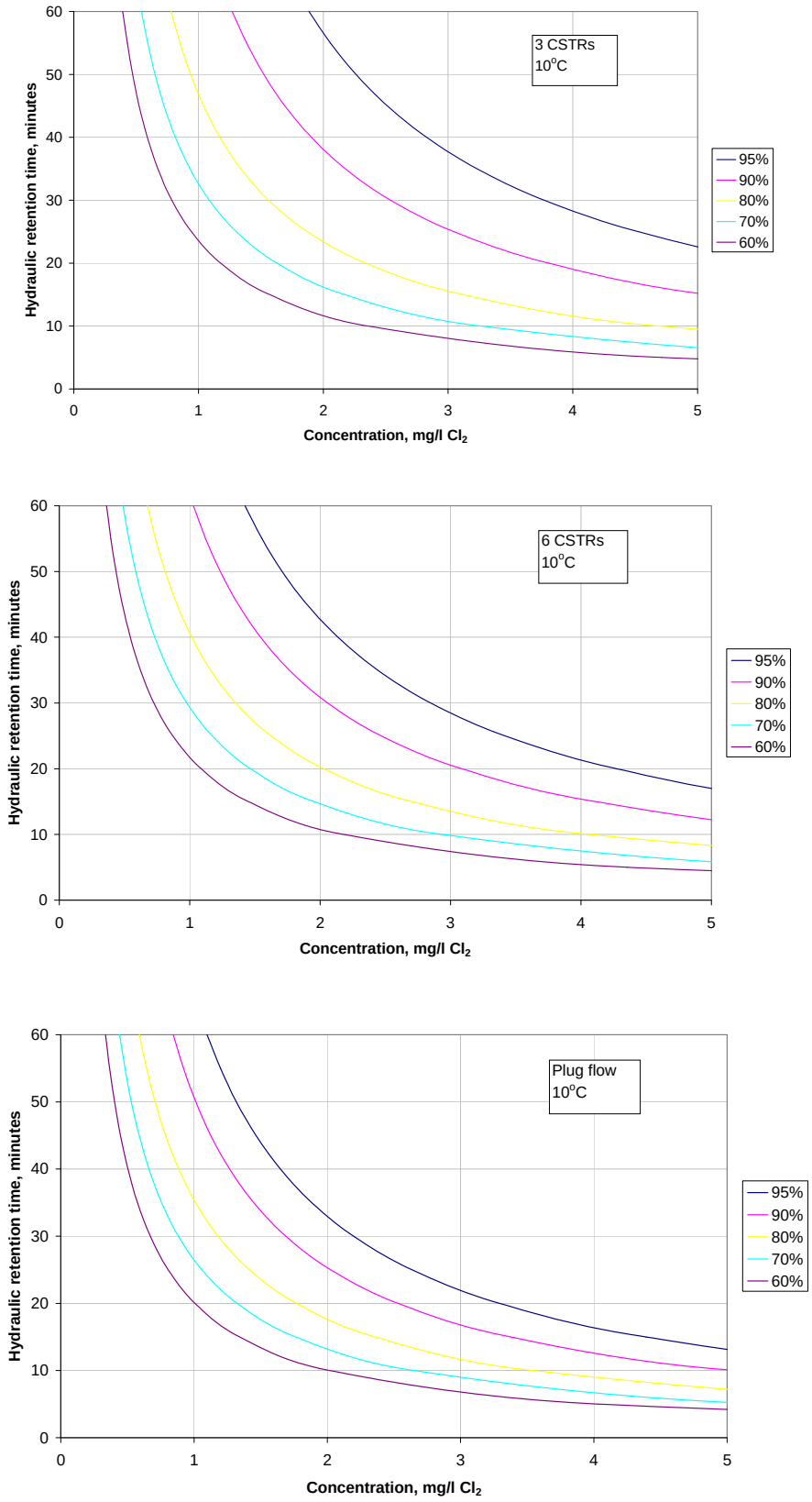

Figure 5-11(L2) Effectiveness of chlorine for m-LR degradation at 10°C

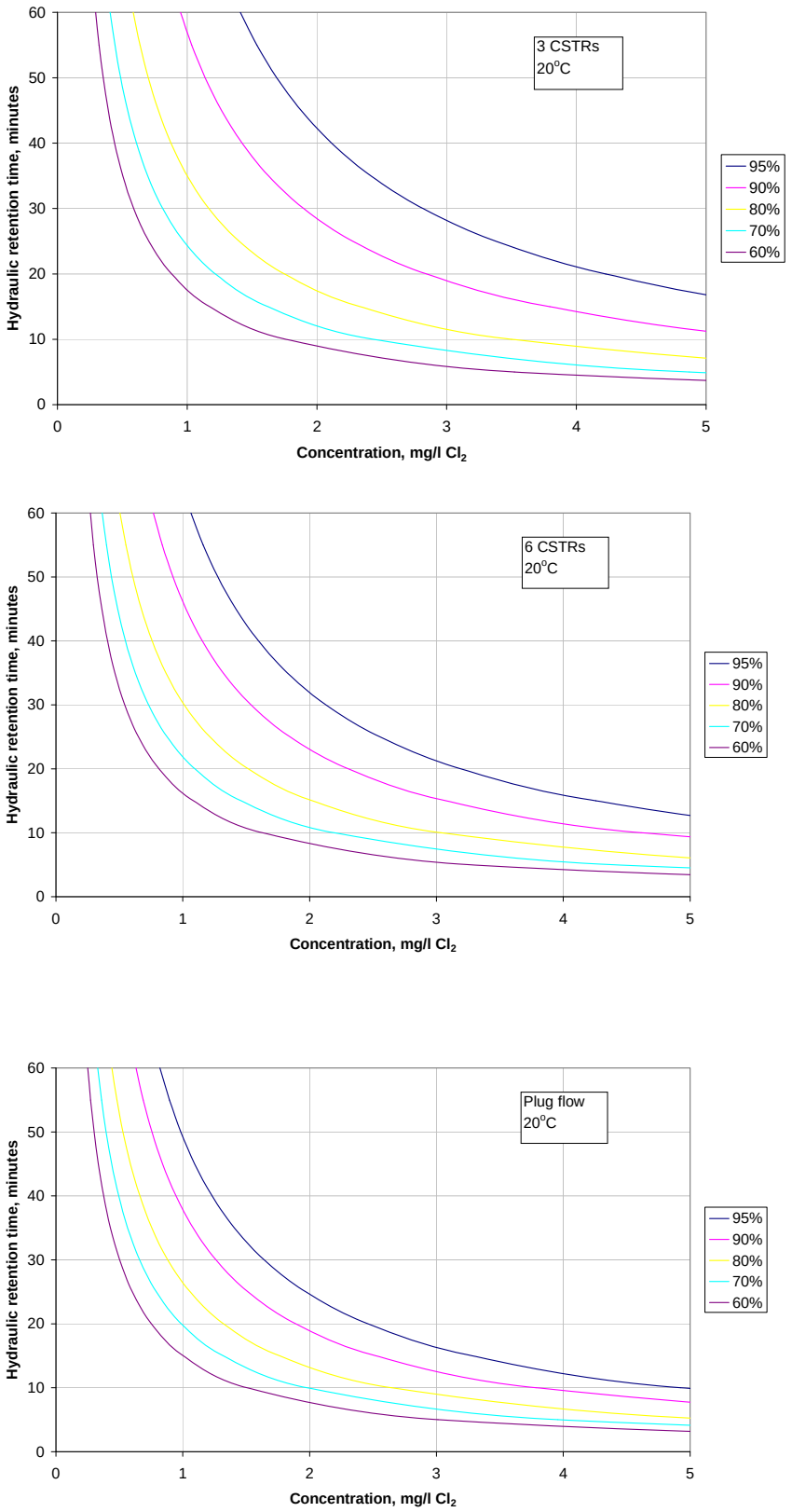

Figure 5-12(L2) Effectiveness of chlorine for m-LR degradation at 20°C

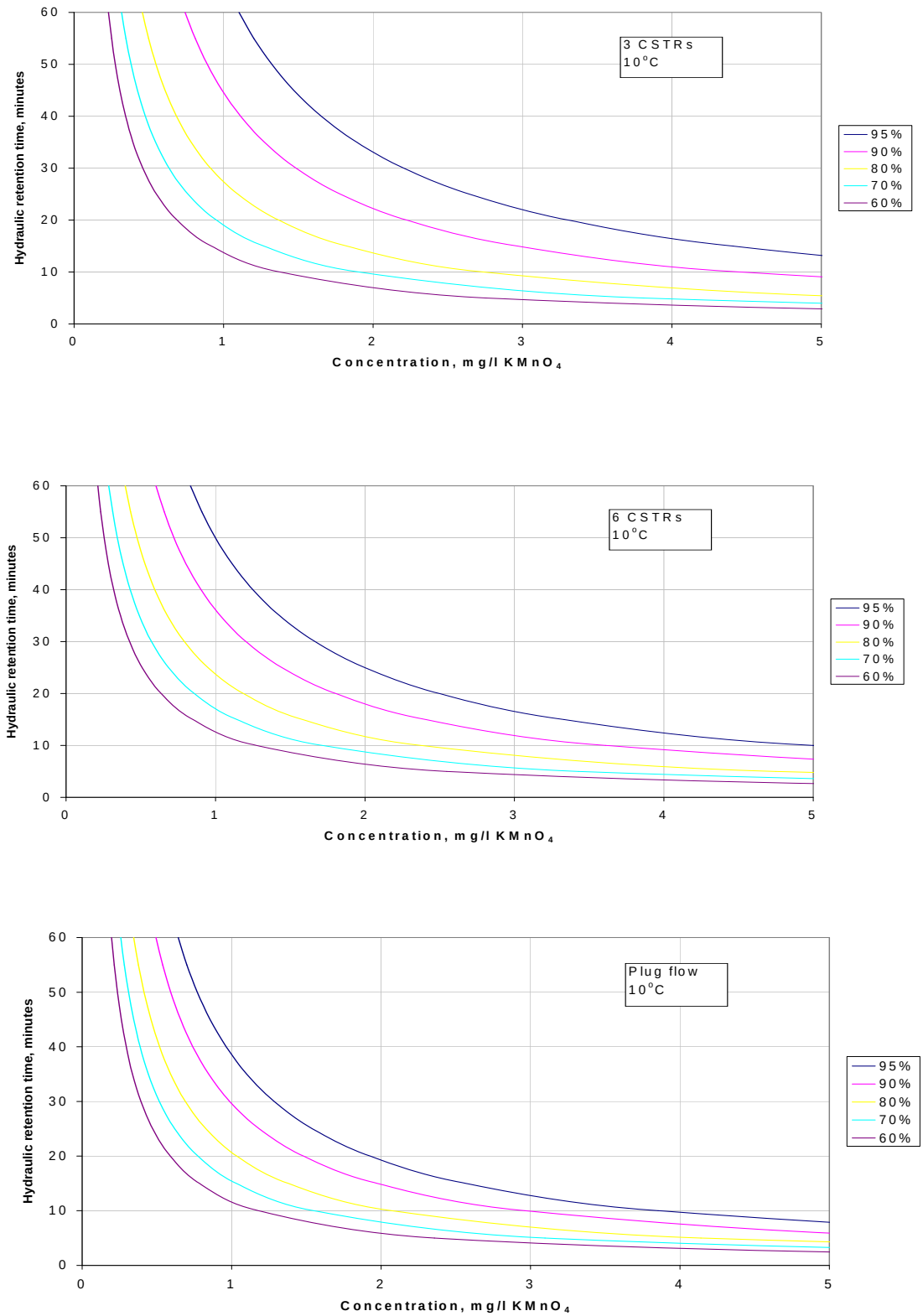

Figure 5-13(L2) Effectiveness of permanganate for m-LR degradation at 10°C

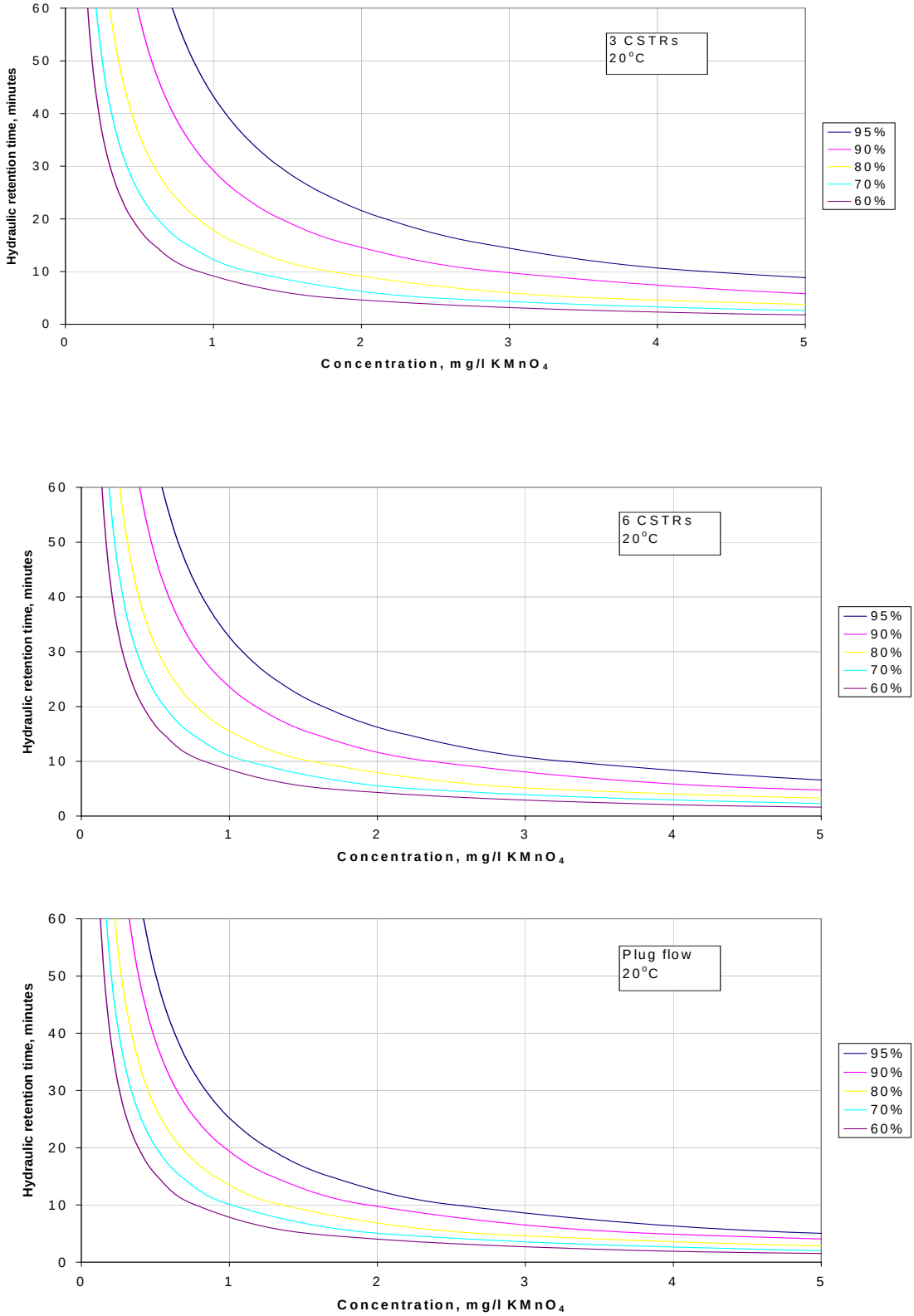

Figure 5-14(L2) Effectiveness of permanganate for m-LR degradation at 20°C

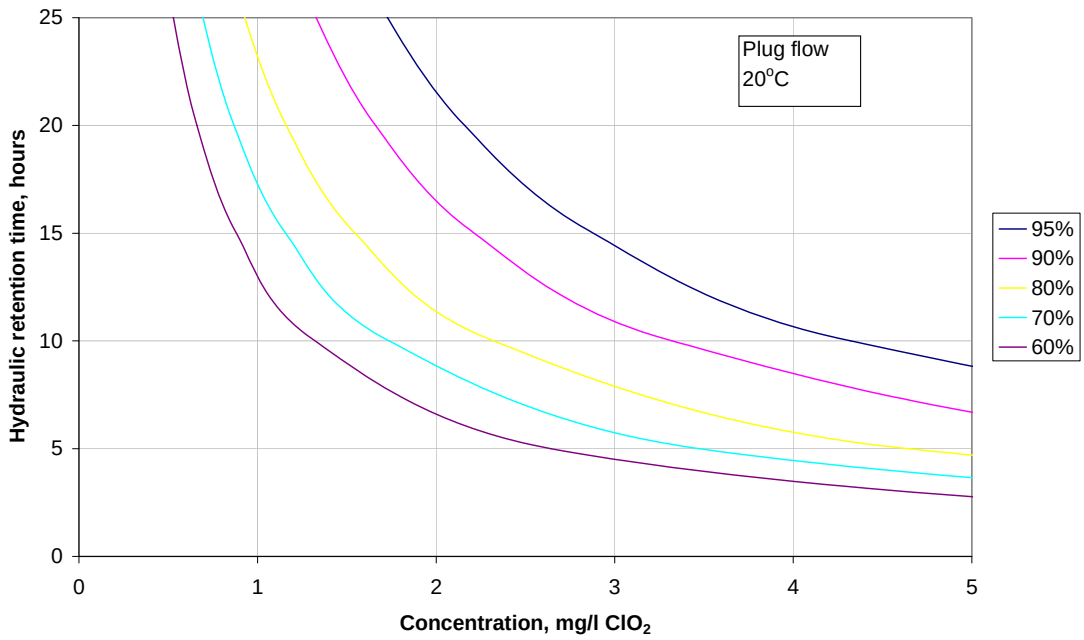

Figure 5-15(L2) Performance of chlorine dioxide for m-LR breakdown

TRACER TESTS FOR OXIDANT CONTACTORS

The value of n of a real tank can be deduced from a tracer test. Lithium chloride is often used, because there is normally little background lithium so small concentrations can be used without needing to take a tank out of service. A chlorine spike is sometimes used to test in-service disinfection contact tanks. If a tank is out of service, other options include sodium chloride (monitored by conductivity) and dye (monitored by UV absorption at the appropriate wavelength). The method is to add an instantaneous dose of tracer to the tank inlet, well mixed with the flow, and monitor for the tracer at the outlet for at least three HRTs. Listing the tracer results as a series of discrete data points of time, t_i, and concentration, C_i, separated by time interval Δt_i (Δt_i does not have to be constant), the value of n is deduced from the mean residence time:

Equation 1

$$\bar{t} \approx \frac{\sum(t_i C_i \Delta t_i)}{\sum(C_i \Delta t_i)}$$

and the variance

Equation 2

$$\sigma^2 \approx \frac{\sum\left(t_i^2 C_i \Delta t_i\right)}{\sum(C_i \Delta t_i)} - \left(\bar{t}\right)^2$$

Then

Equation 3

$$n = \frac{(\bar{t})^2}{\sigma^2}$$

The concept of CSTRs in series requires n to be an integer, so the value found from Equation 3 must be rounded.

An example is given below based on data provided in Table 5-8(L2).

Table 5-8(L2) Example data for calculation of n

t_i (minutes)	Δt_i (minutes)	C_i (mg L^{-1})	$C_i\Delta t_i$	$t_iC_i\Delta t_i$	$t_i^2C_i\Delta t_i$
0	0	0	0	0	0
1	1	0.1	0.1	0.1	0.1
3	2	0.3	0.6	1.8	5.4
5	2	0.5	1.0	5.0	25.0
6	1	0.7	0.7	4.2	25.2
7	1	1.0	1.0	7.0	49.0
9	2	0.9	1.8	16.2	145.8
10	1	0.5	1.0	5.0	50.0
12	2	0.2	0.4	4.8	57.6
13	1	0.1	0.1	1.3	16.9
15	2	0	0	0	0
			Σ ($C_i\Delta t_i$)= 6.7	Σ ($t_iC_i\Delta t_i$)=45.4	Σ $t_i^2Ci\Delta t_i$=375

Mean residence time = 45.4/6.7 = 6.8 minutes
Variance = (375/6.7) – 46.2 = 9.8
Number of CSTRs (n) = 6.8^2/9.8 = 4.7 (=5)

Return to level 1

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